Advances in multi-pollutant control

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Abstract

Pollutants, such as nitrogen oxides (nitrogen dioxide (NO₂) and nitric oxide (NO)), sulphur dioxide (SO₂), sulphur trioxide (SO₃), carbon dioxide (CO₂), mercury (Hg) and particulate matter (PM), are formed when coal is combusted in a power plant boiler. With the concern over the environmental and health consequences of these pollutants, legislation and regulations have been implemented limiting the amounts that can be emitted to the atmosphere. Emission control systems on conventional coal-fired power plants typically employ technologies designed to remove one specific pollutant. These are then combined, in series, to remove several pollutants in order to meet the emission regulations. This report discusses multi-pollutant systems which remove two or more of the principal regulated pollutants (SO₂, NOx, mercury, particulate matter and CO₂) in a single reactor or a single system designed for the purpose. The emphasis is on commercial or near commercial processes, and those that are under active development. Ways to improve the co-benefit removal of oxidised mercury in conventional limestone wet scrubbers, spray dry scrubbers and circulating dry scrubbers are also included. Multi-pollutant systems can have lower capital and operating costs than a series of traditional systems to remove the same number of pollutants. Nevertheless, many of the multi-pollutant technologies rely on by-product sales to be economically competitive. Their footprint is often smaller than conventional single pollutant counterparts treating a similar volume of flue gas, making them easier to install in retrofit applications. Some of the systems use modular designs that ensures easy scalability for larger boilers.
Acronyms and abbreviations

AC  alternating current
CapEx  capital expenditure
CDS  circulating dry scrubber
CFB  circulating fluidised bed
DBD  dielectric barrier discharge
DC  direct current
EB-FGT  electron beam-flue gas treatment
ECO  electro-catalytic oxidation
EPA  Environmental Protection Agency (USA)
EPRI  Electric Power Research Institute (USA)
EPS  Eco Power Solutions (USA)
GSA  gas suspension absorption
ID  induced draught
macf  million actual cubic feet
MATS  Mercury and Air Toxics Standards (USA)
MMBtu  million (10^6) British thermal unit
MP-AQCS  multi-pollutant-air quality control system
MVR  mechanical vapour recompression
NETL  National Energy Technology Laboratory (USA)
NID  novel integrated desulphurisation
NOx  nitrogen oxides (NO + NO₂)
O&M  operation and maintenance
OpEx  operating expenditure
PAH  polycyclic aromatic hydrocarbon
PCD  pulsed corona discharge
PM  particulate matter
ppm  parts per million
PRB  Powder River Basin (USA)
SCR  selective catalytic reduction
SDS  spray dry scrubber
SOx  sulphur oxides (SO₂ + SO₃)
SR  stoichiometric ratio

Conversions

lb/macf to mg/m³ multiply by 16.018
lb/MMBtu to kg/GJ multiply by 0.4299 (that is, 0.4536/1.055)
lb/MMBtu to ppmv NOx (expressed as NO₂, at 6% O₂) multiply by 598
lb/MMBtu to ppmv SO₂ (at 6% O₂) multiply by 430
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I Introduction

In 2010, coal-fired power plants provided around 41% of the world’s electricity. Demand for coal is expected to continue to grow in the emerging economies for the next few years, driven in particular by the power generation industry in China and India. Coal is widely distributed around the world and is the most abundant fossil fuel with reserves of over 1 million tonnes (t) at the end of 2010 or some 140 y at current production rates. Hence coal is likely to remain a major fuel source for some time, although its overall share in the global power generation industry is expected to decrease in the future (IEA, 2012).

Pollutants, such as nitrogen oxides (nitrogen dioxide (NO₂) and nitric oxide (NO)), sulphur dioxide (SO₂), sulphur trioxide (SO₃), particulate matter (PM), mercury (Hg) and carbon dioxide (CO₂) are formed when coal is combusted in a power plant boiler. With the concern over the environmental and health consequences of these pollutants, legislation and regulations have been implemented limiting the amounts of SOx, NOx and particulate matter that can be emitted to the atmosphere. The legislation and regulations have become increasingly stringent over the years, and this continues to be the case today. In addition, regulations are now setting limits for pollutants that were not previously regulated. The United Nations Environment Programme (UNEP), for example, is currently finalising and ratifying a new global legally-binding convention on mercury, the Minamata Convention. The largest source of atmospheric mercury emissions from human activities worldwide is coal combustion. China’s new emission standard for thermal power plants (GB 13223-2011) includes a limit on the amount of mercury (0.03 mg/m³) that can be emitted from coal-fired power plants. The existing state of mercury legislation in the world is reviewed by Sloss (2012). Regulations on CO₂ emissions are also being introduced as a consequence of concerns over the greenhouse effect and climate change. The Canadian Government now requires all new coal-fired power plants built after 1 July 2015 to emit no more than 420 t of CO₂ per GWh of power produced (Cope, 2013). As the need for more stringent controls for power plant emissions increase, so does the need for more cost-effective approaches for reducing these pollutants.

Over forty countries have set limits on the amount of pollutants that can be emitted from coal-fired power plants. The emission limits for two countries and the European Union are compared in Table 1. None of these countries have yet regulated CO₂ emissions. The table shows that emission limits are generally stricter for new build plants than for existing plants. In order to meet these emission regulations, conventional power plants combine several pollutant removal systems, each of which was designed for the removal of a single pollutant. Technologies are now available that can remove two or more pollutants simultaneously in a single system. These multi-pollutant systems could have lower capital and operating costs than a series of traditional systems that remove the same number of pollutants. In addition, multi-pollutant systems are likely to have a smaller footprint, and so may be easier to retrofit on existing power plants.

This report examines multi-pollutant control systems for coal-fired power plants. For the purposes of the report, a multi-pollutant system is defined as one that removes two or more of the principal regulated pollutants (SO₂, NOx, particulate matter, mercury and CO₂) in a single reactor or a single system designed for the purpose. In addition, some technologies that remove a significant portion of a second regulated pollutant as a co-benefit are included. The emphasis is on commercial or near commercial processes, and those that are under active development.

The report begins with wet scrubbing processes, namely the Airborne Process™, NeuStream® and SkyMine® technologies. Limestone wet scrubbers are discussed since they remove oxidised mercury, as well as SO₂. Methods for increasing the mercury removal efficiency are described. Limestone wet scrubbing is the most widely employed flue gas desulphurisation (FGD) technology. It is the system, along with selective catalytic reduction for NOx control, with which multi-pollutant technologies (that
remove SO₂ and NOₓ) are often compared. The next chapter covers semi-dry scrubbing processes, that is, spray dry scrubbers and circulating dry scrubbers. These systems remove SO₂ and, as a co-benefit, mercury. Dry technologies, where no water is consumed, are the subject of Chapter 4. Non-thermal plasma technologies, where the plasma is generated by electron beams, corona discharges or dielectric barrier discharges, are examined in Chapter 5. The following chapter covers gas phase oxidation processes. These processes involve the injection of externally generated ozone to oxidise the relatively insoluble NO into soluble higher oxides, and elemental mercury into soluble mercury oxide. The oxidised compounds, along with SO₂, are then removed by scrubbing (Lextran and LoTOx™) or condensation (Eco Power Solutions’ system). Finally, technologies that cannot be categorised elsewhere are described. The economics of the processes are site-specific, and therefore are discussed only in general terms.

| Table 1 Emission standards for China, European Union and the USA (World Resources Institute, 2012) |
|-----------------------------------------------|------------------|------------------|
|                                               | China            | European Union*  | USA†              |
| NOₓ, mg/m³                                   |                  |                  |                   |
| new plants                                  | 100              | 500 until 31 Dec 2015, then 200 | 117              |
| existing plants                             | 100 (built 2004-11) | 500 until 31 Dec 2015, then 200 | 117 (built after 2005) |
|                                               |                  |                              | 640 (built 1978-96)   |
| SO₂, mg/m³                                   |                  |                  |                   |
| new plants                                  | 100              | 200              | 160 (built after 2005) |
| existing plants                             | 200 (28 provinces) | 400              | 160 (built 1997-2005) |
|                                               | 400 (4 provinces with high S coals) | | 640 (built 1978-96)   |
| PM, mg/m³                                   |                  |                  |                   |
| new and existing plants                      | 30               | 50, with an exception of 100 for low quality coal, such as lignite | 22.5              |
| Mercury, mg/m³                               |                  |                  |                   |
| new plants                                  | 0.03             | –                | 0.001 (bituminous, gangue) |
|                                               |                  |                  | 0.005 (lignite)      |
| existing plants                             | 0.03             | –                | 0.002 (bituminous, gangue) |
|                                               |                  |                  | 0.006 (lignite)      |

* for power plants >500 MW in size
† units in the standards have been converted to concentrations
This chapter covers wet scrubbing processes where the scrubbing liquid is typically sprayed into the flue gas in an absorber tower to remove the targeted pollutants. It begins with limestone wet scrubbers since some of the newer multi-pollutant systems are compared to this technology, often in combination with selective catalytic reduction (SCR) for NOx control (termed wet FGD + SCR). Three technologies that are at the demonstration or commercial stage are then described. Other processes that include a wet scrubbing component include the ECO™ system (see Section 5.3.1), Lextran (see Section 6.2) and LoTOx™ (see Section 6.3).

2.1 Limestone wet scrubbers

Wet FGD systems were developed in the late 1960s primarily to remove SO2 from flue gas, but as a co-benefit remove oxidised mercury and particulates. The limestone wet scrubber system is the most widely deployed FGD technology, and has been installed on units burning low to high sulphur coals. Although other sorbents, such as lime, magnesium oxide, ammonia, and sodium carbonate, are used in wet scrubbers, limestone (calcium carbonate) is normally the cheapest sorbent and is available in large amounts in many countries. Wet scrubbers typically remove 95% to >99% of the SO2, up to ~60% of SO3, >98% of HCl and HF, >70% particulates, 75–99% of oxidised mercury, and at least 50% of total mercury, depending on the type of coal burned and power plant operating conditions (Klingspor, 2012; Moretti and Jones, 2012; Moss, 2010; Sloss, 2008). A saleable by-product, gypsum, is produced.

A typical wet limestone FGD system consists of a limestone preparation, storage and handling system, a FGD spray tower absorber, a by-product dewatering system, and a wastewater treatment system. The absorber can be a co- or counter-current flow spray tower, with or without internal packing or trays. It is usually installed downstream of the particulate control device. In the USA, the flue gas enters the absorber at a temperature of around 120–180ºC (EPRI, 2007). The temperature depends on a number of factors relating to the boiler arrangements, coal type and the load on the generator. European practice is to use a heat exchanger prior to the absorber, whereby the flue gas is cooled to around 80–90ºC. Passing through the scrubber, with all the evaporation taking place, it is further cooled to ~50ºC. The flue gas is then reheated in the heat exchanger (exchanging with the incoming gas) to ~90ºC before being emitted (Couch, 2005).

A common type of absorber is the counter-flow open spray tower (see Figure 1) where the limestone slurry is pumped through banks of spray nozzles to atomise it into fine droplets and uniformly contact the gas. The droplets absorb SO2 from the flue gas, facilitating reaction with the limestone. HCl present in the flue gas is also absorbed and reacts with the limestone to form calcium chloride. Oxidised mercury is water-soluble and is absorbed in the aqueous slurry. Some of the water in the spray droplets evaporates, cooling the gas and saturating it with water. The cleaned flue gas passes through the mist eliminators to remove the entrained droplets and is emitted to the atmosphere via the cooling tower, a wet stack or a dry stack after reheating. The spent sorbent slurry collects in the reaction tank at the bottom of the absorber. Compressed air is commonly injected into the reaction tank to oxidise the hydrated calcium sulphite into hydrated calcium sulphate (gypsum, CaSO4·2H2O). This oxidation step is termed forced oxidation. Complete oxidation is ensured by maintaining a low pH. Limestone slurry is added to the reaction tank to control the pH and replenish the limestone consumed in the process. A slurry recycle system recirculates the limestone sorbent from the reaction tank to the spray nozzles. A bleed system removes the appropriate amount of gypsum and solid wastes from the reaction tank to maintain process equilibrium, and transports the slurry to the gypsum processing system. The gypsum is dewatered and processed to produce a saleable quality product or is sent for landfill disposal.
The principal reactions occurring in limestone wet scrubbers with forced oxidation are:

\[
\begin{align*}
\text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_3 \\
\text{CaCO}_3 + \text{H}_2\text{SO}_3 & \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} + \text{CO}_2 \\
\text{CaSO}_3 + \frac{1}{2}\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O}
\end{align*}
\]

Unfortunately, CO₂ is produced and is emitted with the scrubbed flue gas, thus adding to CO₂ emissions from the power plant.

Limestone wet scrubbers often use an organic acid additive to enhance SO₂ removal. State-of-the-art scrubbers have a high SO₂ removal efficiency (>99%) when firing low to high sulphur coals, but do not capture significant amounts of SO₃. Since the flue gas is completely saturated in the scrubber, nearly all the SO₃ or sulphuric acid vapour in the flue gas is condensed into aerosol droplets which are too small to be efficiently captured. Fifty per cent or more of these droplets pass through the scrubber, and can cause plume opacity problems with high sulphur coals. If air pollution regulations require SO₃ removal then it could be captured (adding to both cost and pressure losses) by injecting an appropriate sorbent (such as trona) into the ductwork upstream of the ESP/fabric filter. The sorbent reacts with SO₃ to form a solid compound which is captured in the particulate collector (Carpenter, 2012). Otherwise a wet ESP can be installed after the wet scrubber to capture SO₃ (as sulphuric acid). The wet ESP additionally removes the fine particulates that have passed through the upstream ESP/fabric filter and scrubber. The scrubber captures over 70% of the particulates that pass through the ESP/fabric filter. The DynaWave®/membrane wet ESP combines a reverse jet scrubber with a membrane ESP in one modular unit. The membrane ESP can be operated in the condensing mode, which also enhances particulate collection (Caine and Meyer, 2009).

The amount of mercury captured in the wet scrubber is dependent on a number of factors, principally the type of coal, the equipment configuration and operational factors. A survey of US coal-fired power plants conducted by the US EPA showed that power plants with a cold-side ESP (installed after the air heater) and wet FGD system captured, on average, 81% of mercury when US bituminous coal was fired, 29% with subbituminous coal and 48% with lignite (UNEP, 2010). Plants with hot-side ESPs (upstream of the air heater) and wet FGD removed lower amounts of mercury: 46% with bituminous coals and 20% for subbituminous coals. Plants with fabric filters and wet FGD achieved 98% mercury removal when firing bituminous coals. Mercury capture is higher with fabric filters than ESPs due to continuing reactions in the filter cake. Combustion of non-US coals may result in different mercury capture rates for the same type of coal, which may be due to differences in composition.
The strongest factor affecting mercury removal was the type of coal burnt, with units firing subbituminous coal and lignite showing significantly lower mercury capture than similarly equipped bituminous coal-fired units. The higher chlorine content in bituminous coal results in a higher content of oxidised mercury (Hg$$^{2+}$$) at the scrubber inlet because of the oxidation of elemental mercury (Hg$$^0$$). Elemental mercury passes through the wet scrubber whilst gaseous Hg$$^{2+}$$ is water-soluble and is removed. However, under some conditions, Hg$$^{2+}$$ can be reduced back to its elemental form and re-emitted from the scrubber. This re-emission limits the amount of mercury that can be captured in wet scrubbers. Nearly all the particulate-bound mercury (Hg$$^0$$) is captured in the upstream ESP or fabric filter.

Techniques to enhance mercury capture in wet scrubbers involve increasing elemental mercury oxidation and/or inhibiting its re-emission. The occurrence and extent of mercury re-emission from wet scrubbers depends on the FGD chemistry. Commercial additives are available, such as Nalco’s MerControl 8034 and Babcock & Wilcox Power Generation Group’s Absorption Plus (Hg)TM, that prevent mercury re-emission by reacting with the dissolved oxidised mercury to form an insoluble chemical species that is subsequently precipitated and removed from the scrubber. Some additives do not affect the gypsum purity, enabling the gypsum to be sold (provided there is a local market). Additives that can be added to the scrubber (often with the recirculated slurry) to oxidise elemental mercury and so enable the scrubber to directly capture Hg$$^0$$ have been investigated. Some of the oxidants, such as sodium chlorite, can also prevent the reduction of oxidised mercury, and hence mercury re-emission (Hutson and others, 2010; Ochoa-González and others, 2013). Since these often react with SO$$_2$$ and sulphites, it seems unlikely that their use in spray tower scrubbers will work without excessive additive consumption. For mercury oxidation within the scrubber, oxidants resistant to SO$$_2$$ deactivation will need to be developed (Martin and others, 2009).

Increasing the oxidation air flow rate may, in some cases, inhibit mercury re-emission without the use of chemical additives. Mercury removal efficiency rose from 63% to over 92% at one US plant operating limestone forced oxidation wet scrubbers using this technique, but sometimes increased mercury re-emission at another plant (Cheng and others, 2013).

Commercial oxidants are available that can be added at different points upstream of the scrubber to help form more oxidised mercury that can be captured in the scrubber. To comply with the US Mercury and Air Toxics Standards (MATS), 90% or more of the mercury must be in the gaseous oxidised form at the scrubber inlet (Senior, 2012). The oxidants can be added to the coal (such as KNX™ and MercPlus™) or injected into the furnace (for example, NH$$_4$$Cl), at the economiser outlet or elsewhere in the ductwork (Moretti and Jones 2012; Morris, 2012; Senior, 2012; Sloss, 2008, 2012). The simplest method for increasing the amount of oxidised mercury at the scrubber inlet is by coal selection and blending, for example, by increasing the chlorine content (Sloss, 2008).

Mercury can also be oxidised over catalysts. The catalyst may be placed in the flue gas specifically for this purpose or may already be installed, such as in an SCR unit. An SCR unit may increase the amount of oxidised mercury up to about 85% (UNEP, 2010). SCR combined with wet scrubbers can generally reduce mercury emissions to below 2 µg/m$$^3$$ (Sloss, 2012). Obviously there will be some exceptions to the rule, especially at plants firing low rank coals. It would also mean operating the SCR unit throughout the year. Oxidants can be injected upstream or into the SCR to augment the formation of oxidised mercury. However, injection of oxidants, especially halogen-based ones, into the furnace, SCR or ductwork adds to the plant’s operating costs, could cause corrosion problems in downstream equipment, and may contaminate the fly ash. Loss of ash sales will mean a loss in revenue and additional disposal costs. Installing a catalyst or injecting the oxidant downstream of an ESP/fabric filter would leave fly ash quality unaffected. Pilot-scale tests at three US power plants, firing low sulphur bituminous coal, subbituminous coal or lignite, oxidised over 90% of the mercury when using a gold- or palladium-based honeycomb catalyst. Oxidised mercury removal efficiencies of ≥95% were achieved in the downstream wet scrubber when operated in the limestone forced oxidation or lime inhibited oxidation modes. Total mercury removal was 87–93% in several test runs (Blythe and others, 2011).
A combination of techniques, such as coal additive and oxidant injection, may be needed at some power plants to meet mercury emission regulations. Otherwise a mercury specific technique can be applied, such as injection of activated carbon, brominated activated carbon or ‘concrete compatible’ sorbents into the ductwork between the air heater and particulate control device. The solid reaction products are collected in the particulate collector, and so there is little mercury capture in the wet scrubber.

Mercury passing through a wet scrubber can be captured in systems, such as the Gore® mercury control system, which would also eliminate the mercury re-emission issue. The Gore® system uses a sorbent polymer composite in a fixed bed system to capture both elemental and oxidised mercury, and, as a co-benefit, additional SOx. The modules can be installed within the wet scrubber after the mist eliminators, or downstream in a separate housing (Kolde and Souder, 2012). A pilot-scale demonstration on a flue gas slipstream from the limestone wet scrubber at the Yates power plant in Newnan, GA, USA, removed 90% of the remaining mercury and 50–70% of the remaining SO2 over the six-month test period (Morris, 2012).

NOx could be removed in wet scrubbers provided NO, which accounts for more than 95% of the total NOx in flue gas, is first oxidised to water-soluble higher nitrogen oxides. One option is to add a soluble oxidant to the scrubber liquor. Otherwise NOx can be oxidised by injecting ozone or another oxidant into the ductwork upstream of the wet scrubber. This forms part of the multi-pollutant processes, such as Lextran (see Section 6.2), LoTOx™ (see Section 6.3) and NeuStream® (see Section 2.3), although some of these technologies may use a sodium-based scrubber instead of a limestone scrubber. The ozone is injected after the particulate control device in these systems. FMC Corporation’s PerOxide technology injects hydrogen peroxide (H2O2) into the duct between the economiser and air heater where the temperature is between ~300–600°C. Over 80% of the NO is oxidised to NO2 (Crynack and others, 2011). Oxidation of SO2 to unwanted SO3 is suppressed at the elevated injection temperature. Elemental mercury is oxidised, increasing the efficiency of mercury capture in wet scrubbers. However, NO2 removal in limestone wet scrubbers is not very efficient, although the higher-order nitrogen oxides are much more soluble than NO2 and can be almost completely removed by wet scrubbing. The proportion of higher-order nitrogen oxides relative to NO2 increases at higher oxidant dosing rates, but at a cost.

Various additives, such as sodium sulphite, sodium hydroxide, sodium chlorite, magnesium sulphate and potassium permanganate, have been investigated to enhance the removal of NO and NO2 (and Hg). One way of promoting NOx removal is to increase the dissolved sulphite concentration, a reaction product in limestone wet scrubbers. This can be achieved by adding sulphite compounds to the scrubbing solution, or by adding a compound, such as thiosulphate, to inhibit sulphite oxidation. Sodium-containing buffer additives, such as sodium formate, could replace additives, such as dibasic acid, to help elevate the dissolved sodium concentration (Crynack and others, 2011). Removal efficiencies of ~70% for NO2 and 98% for SO2 were achieved with the addition of sodium sulphite in bench-scale tests, and could be applied to limestone inhibited oxidation scrubbers (Crynack and others, 2011). Ferrous sulphate (FeSO4) gave the highest NO2 removal efficiency (>90%) of the additives tested by Wang and others (2012). But its consumption rate was high. Ammonium sulphate ((NH4)2SO4) had a similar removal efficiency and a lower consumption rate. Nearly 100% of SO2 was also removed.

The addition of low levels of sodium chlorite (NaClO2, ~0.005 M) into the scrubbing solution removed nearly all the mercury and NO, and ~50% of NOx (as NO2) in bench-scale experiments when operating in the forced oxidation mode. However, lower removal rates were achieved in the pilot-scale tests (around 70% Hg, 30% NO and 15% NOx). SO2 removal efficiency was nearly 100% in all the tests. Injecting sodium chlorite upstream of the wet scrubber captured all the SO2, Hg and NO, and ~90% of NOx (Hutson and others, 2010; Krzyzynska, 2012; Krzyzynska and Hutson, 2012). Bench-scale tests in which a composite absorbent based on sodium chlorite was added to the scrubber solution (~4.1 M) removed 100% of SO2 and ~95% of NO (NO2 production was suppressed) under
optimal conditions. The removal efficiency was about the same as using sodium chlorite alone, but at a lower absorbent cost (Zhao and others, 2011a).

Limestone wet scrubbers have a high reliability and good turnaround capability. Single absorber module sizes of over 1000 MW are available. However, the scrubbers increase a plant’s CO₂ emissions as CO₂ is a by-product of the desulphurisation process. Moreover, plume opacity problems can occur due to SO₂/H₂SO₄ aerosol droplets passing through the scrubber. Installing regenerative heat exchangers upstream of the particulate control device can control SO₂/H₂SO₄ emissions through condensation on the fly ash, as well as reducing FGD make-up water consumption. Regenerative heat exchangers are commonly installed in coal-fired power plants in Japan and Europe, although they are expensive and can have high operating and maintenance costs.

Auxiliary power consumption of wet scrubbers is around 1.2–1.5% when burning low sulphur coals and 1.5–2% or more with high sulphur coals (Adamson, 2008). This is principally due to the additional ID fan power consumption to compensate for the pressure drop across the absorber and the power requirements for the slurry recirculation pumps. Make-up water consumption is high at around 250 L/MW·h or 2162 L/min in a 500 MW subcritical power plant and some 220 L/MW·h or 1900 L/min in a 500 MW supercritical power plant when firing 3 wt% sulphur (dry basis) bituminous coal (Klett and others, 2007). The wastewater treatment plant is relatively complex and expensive as several stages of treatment are needed to meet discharge regulations. The complexity and cost is likely to increase if future regulations mandate zero liquid discharge in order to achieve a sufficient quality to enable its reuse in the power plant. The presence of sulphuric acid and other corrosive compounds means that the absorber vessel is manufactured from more expensive corrosion-resistant materials. Similarly, corrosion-resistant materials are required in the downstream equipment and ductwork due to the presence of corrosive chlorides and sulphuric acid in the flue gas exiting the mist eliminators. Reheating the flue gas to above its dew point before it is emitted can help to minimise corrosion. The absorbers are also handling large volumes of abrasive slurries.

Capital, operation and maintenance (O&M) costs are relatively high due to some of the factors discussed above. A 2008 survey covering 78 retrofitted scrubbers in the USA found that the average capital cost for just the FGD system was 404 US$/kW for units below 300 MW, 349 US$/kW for 300–599 MW units, 284 US$/kW for 600–900 MW units and 290 US$/kW for units over 900 MW. The FGD system included the absorber vessel, reagent preparation system, FGD waste disposal and the balance-of-plant costs. The cost of the wastewater treatment system, new stack and ductwork, and other project costs for boiler cleaning or major electrical upgrades were excluded. All the FGD units used limestone forced oxidation technology, with almost two-thirds being spray type and a third were jet bubbling reactors (Sharp, 2009). Installing a limestone wet scrubber at the 475 MW (net) PRB-fired Big Stone power plant Unit 1, near Big Stone City, SD, USA, would have a capital cost of US$171,800,000 and annual O&M costs of 9,600,000 US$/y (calculated for year 2009) (Otter Tail Power, 2009). The gypsum by-product can be sold to offset costs. But the market for gypsum is limited, largely by proximity to the end market and the availability of cheap transport.

2.2 Airborne Process™

The Airborne Process™, developed by Airborne Clean Energy Ltd in Calgary, AB, Canada, combines dry sorbent (sodium bicarbonate) injection with enhanced wet sodium scrubbing and advanced chemical oxidants to remove SOₓ, NOₓ, mercury and other heavy metals, and acid gases (such as HCl, HF, H₂S) from flue gas. The sodium bicarbonate is regenerated and a saleable ammonium sulphate and ammonium nitrate fertiliser is produced. Pilot-scale and small-scale demonstration tests have indicated that the Airborne Process™ could remove 99.9% of SO₂ and SO₃, 99% of NOₓ and 99% of mercury (Mortson and Xia, 2006).

Both the sodium bicarbonate injection and wet sodium carbonate scrubbing technologies are in
operation at coal-fired power plants worldwide. The proprietary sodium bicarbonate regeneration component has been demonstrated at the commercial sodium sulphate mine in Ormiston, SK, Canada. The sodium sulphate was upgraded to commercial-grade sodium bicarbonate and ammonium sulphate in the 16.3 t/d demonstration unit. However, the integrated Airborne technology has not yet been demonstrated at commercial-scale. It has been demonstrated on a 5 MW slipstream at Kentucky Utilities’ Ghent station near Carrollton, KY, USA, that operated between January and July 2003. The planned full-scale demonstration at Peabody Energy’s 300 MW Mustang Energy Project near Milan, NM, USA, did not go ahead. Peabody Energy was unable to secure an air permit from the New Mexico Government (Dene and others, 2008a) over CO2 emissions and withdrew their application. The current emphasis for marketing the Airborne Process™ is in China, where Airborne China Ltd expects to complete the first two commercial projects by April 2014 (Morton, 2013).

The Airborne Process™ consists of four steps, namely dry sorbent injection, wet scrubbing, oxidant wash and sorbent regeneration/fertiliser production (see Figure 2). In the first step, dry sodium bicarbonate is injected into the flue gas downstream of the particulate control device. The sodium bicarbonate undergoes thermal decomposition, which results in the formation of porous sodium carbonate particles that have a large surface area and are highly reactive to acid gas species. Sodium carbonate formed from sodium bicarbonate in this way has been found to be a significantly better adsorbent than commercial sodium carbonate. Sulphur dioxide and sulphur trioxide react with the sodium carbonate and bicarbonate to form sodium sulphate, as follows:

\[
2\text{NaHCO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{Na}_2\text{CO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2
\]

\[
2\text{NaHCO}_3 + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{Na}_2\text{CO}_3 + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2
\]

Some of the nitric oxide (NO) is converted to NO2 in the presence of the sodium bicarbonate particles and SO2, and some is reduced to nitrogen. The NO and NO2 react with sodium bicarbonate to form sodium nitrate and sodium sulphate, as follows:

\[
2\text{NaHCO}_3 + \text{SO}_2 + \text{NO} + \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{NO}_2 + \text{H}_2\text{O} + \text{CO}_2
\]

\[
2\text{NaHCO}_3 + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{NaNO}_3 + \text{H}_2\text{O} + 2\text{CO}_2
\]
The decrease in NOx at this stage is a function of the amount of SO2 removed, as well as other factors. The flue gas and sorbent then pass into a multi-stage absorber tower (wet scrubber). The sodium sulphate and sodium nitrate particles are absorbed into the solution that is flowing downwards. The flue gas continues to flow upwards where it comes into contact with the sodium carbonate scrubbing solution to remove the remaining SOx. Oxidants are injected through spray nozzles into the zone at the top of the absorber to remove additional NOx and mercury, which are captured in a different solution. The spent sulphite/sulphate solution collects in the tank at the bottom of the absorber. If required, air can be injected into the tank to oxidise the sulphite into sulphate.

Both solutions from the wet scrubber are then treated by precipitation and filtration to remove the heavy metals and particulate matter, which are then sent for disposal. The purified sodium sulphate/nitrate solution is combined with the filtered oxidant solution, evaporated to the desired concentration and sent to the regeneration unit. Here, the sodium sulphate/nitrate is reacted with ammonium bicarbonate to form ammonium sulphate, ammonium nitrate and sodium bicarbonate. The sodium bicarbonate precipitate is separated and dried before reinjection into the scrubbing system. The ammonium sulphate and ammonium nitrate are individually crystallised out of the solution, and then granulated and mixed with a binder to produce commercial grade fertilisers (a proprietary process termed pan granulation).

The regeneration can also be accomplished by reacting ammonia and carbon dioxide gases with the sodium sulphate/nitrate solution. The flue gas, stripped of SOx, NOx and mercury, could be used as the CO2 source. As an option, potassium chloride and calcium oxide can be added to the ammonium sulphate solution to produce potassium sulphate fertiliser, and the ammonia that is formed is recycled. This reduces the need for ammonia feedstock, which is expensive and difficult to store (Johnson and others, 2005; Mortson and Telesz, 2001; Mortson and Xia, 2006; Washington Group International, 2005). In the Chinese projects, ammonia is being used in the form of ammonium bicarbonate, which eliminates the transportation and storage issues of ammonia (Mortson, 2013).

The development of the Airborne Process™ has overcome two perceived drawbacks of conventional sodium scrubbing. Firstly, the high cost of the sorbent is reduced by regenerating the sodium bicarbonate reagent. Conventional sodium scrubbing at the Jim Bridger, Naughton and Reid Gardner power plants in the USA, is only economic because a waste product sodium material from a manufacturing process is used (Dene and others, 2008a). Secondly, the production of granular ammonium sulphate and ammonium nitrate fertilisers means that the cost and problems of landfill disposal of the sodium sulphate/nitrate by-products are avoided, whilst providing an additional revenue source for the utility. Sodium sulphate is soluble and therefore could leach into the environment. Some solid wastes, albeit a smaller quantity, are still generated (from the purification of the sodium sulphate/nitrate solution) that require landfill disposal. The wastes contain mercury and other heavy metals, and particulate matter. However, these commercial advantages come at the cost of added complexity.

It is claimed that the Airborne Process™ can remove over 99% of SOx, NOx and mercury, making it one of the more efficient multi-pollutant control technologies. This is achieved at lower capital and operating costs than separate conventional pollutant control technologies (SCR, limestone wet scrubber, wet ESP and activated carbon injection) (Mortson and Xia, 2006; Washington Group International, 2005). Water consumption is lower than a limestone wet scrubber removing a comparable amount of SO2 from the flue gas. Most of the water loss is from evaporation in the wet sodium scrubber. The smaller footprint also makes it more easily retrofitted. The parasitic energy consumption of the process can be high unless waste heat sources are available and integrated with the overall plant. Total parasitic power consumption is typically around 3% (Mortson, 2013). Saturated steam is required in the regeneration system for evaporation, steam stripping and drying. Thermal energy integration is feasible between the regeneration unit and the FGD system that will reduce steam demands. Additionally, mechanical vapour recompression evaporation systems can almost eliminate the steam demands. Low level heat recovery is possible upstream of the Airborne absorber.
It could be used to offset the heating duty in the regeneration system, reheat the flue gas (if desired) or integrated into the boiler circuit as an additional economiser. In the case of integration, the plant efficiency could be increased by 1–2% (Mortson and Xia, 2006).

Installing the Airborne Process™ would increase the power plant’s CO₂ emissions by about 1% since CO₂ is emitted in the reactions of SOx and NOx with the sodium bicarbonate/carbonate regent (see the reactions given above). This occurs if the CO₂ is not recovered from the flue gas for use in the regeneration step (with ammonia). The additional 1% CO₂, though, needs to be recovered in order to regenerate the sodium bicarbonate reagent. In the Chinese plants, ammonium bicarbonate is used as the CO₂ chemical source for the regeneration stage. The flue gas CO₂ could be captured in an additional stage, if future regulations require the installation of CO₂ control systems or the economics dictate this step. The low SOx, NOx and particulate levels in the flue gas would enable this to be achieved more efficiently and at a lower cost, since no additional polishing stage is required to remove these pollutants. Some of the captured CO₂ could then be used in the regeneration unit. Airborne Clean Energy are currently working on direct and indirect CO₂ removal systems (Mortson, 2013). For more information about the Airborne Process™ see www.airbornecleanenergy.com.

2.3 NeuStream® technology

NeuStream®-MP, a multi-pollutant system developed by Neumann Systems Group, removes SO₂, HCl, oxidised mercury and particulates in a dual-alkali FGD system (NeuStream®-S), NOx with upstream ozone injection (NeuStream®-N), and CO₂ with the addition of the NeuStream®-C system. Saleable by-products are produced. Up to 97% SO₂, 98% HCl, <95% particulates, >90% oxidised mercury (~80% total mercury), >90% NOx and 70–90% CO₂ (with piperazine solvent) can be achieved when burning low or moderate sulphur coals (Fredell and others, 2012; Kladder and others, 2011). The NeuStream®-S FGD system has been demonstrated on a 20 MW pilot unit treating a slipstream from the Martin Drake Unit 7 in Colorado Springs, CO, USA. A SOx removal efficiency of 90–96% was achieved on low sulphur (<0.5%) subbituminous coal (Kladder, 2010). The pilot tests were validated by the Electric Power Research Institute (EPRI), who concluded that the system could be easily scaled up for larger plants. A full-size NeuStream®-S system is being installed at the Drake Units 6 (85 MW gross) and 7 (142 MW gross). A 0.28 MW pilot test at GenOn Energy’s Shawville power plant burning higher sulphur bituminous coal, and with ozone injection for NO oxidation, removed 81% of NOx (on a reduced slipstream flow of 0.22 MW) and up to 96% SO₂ (Neumann Systems Group, 2013a). The company is in the midst of a US Department of Energy/National Energy Technology Laboratory (DOE/NETL) funded 0.5 MW carbon capture pilot programme, and has just submitted a US$18.75 million grant application to the DOE/NETL for its carbon capture technology to be hosted at the Martin Drake facility (Neumann Systems Group, 2013b).

Ozone is injected into the flue gas after it exits the ESP or fabric filter to oxidise NOx and mercury into water soluble oxides. The flue gas then enters the patented cross-flow, flat jet scrubber (NeuStream®-S system) where SOx, NOx, mercury oxides and other acid gases are absorbed into the sprayed sodium-based alkali solution (see Figure 3). The solvent is then regenerated, typically with lime (calcium oxide or hydroxide), and recycled back to the scrubber. The precipitated calcium sulphites or calcium sulphates (gypsum) are dewatered and either sent to landfill or sold.

The dual-alkali process can be operated in either an inhibited mode where oxidation of sodium sulphite to sodium sulphate is purposely inhibited, or in an oxidised mode where the oxidation of sodium sulphite to sodium sulphate is promoted. Since the oxidation levels in the scrubber are a function of SOx concentration in the flue gas, the oxidised mode is better suited for low sulphur (<1.5% S) coal applications, whilst the inhibited mode is preferred for high sulphur (>1.5% S) coals. A softening system to precipitate calcium (as calcium carbonate) with flue gas carbon dioxide is included in the oxidised mode, as shown in Figure 3. This lowers the calcium content in the return solvent to below 10 ppm, eliminating nozzle clogging concerns.
The NeuStream®-C system is based on the same patented technology as NeuStream®-S, and has been tested at the Energy and Environmental Research Center’s (EERC) Combustion Test Facility in Grand Forks, ND, USA. The system consisted of a three-stage absorber and four-stage stripper, treating a 4.5 m³/min coal-derived flue gas stream (Brasseur and Awtry, 2012). The piperazine solvent captured more CO₂ than monoethanolamine (MEA); around 80–90% of CO₂ was captured. In addition, the thermal regeneration energy requirements for 8 M piperazine are 10–20% less than for 7 M MEA (Awtry and Klein, 2013). The NETL has partly funded a 0.5 MW pilot test of a three-stage NeuStream®-C system at the Martin Drake Unit 7 (grant awarded Aug 2011), where NeuStream®-S is used to clean the flue gas prior to its treatment in the CO₂ capture and regeneration system.

The NeuStream® technology is in the early stages of commercialisation. It has several advantages over conventional FGD and CO₂ systems. The scrubber is around a tenth of the size of spray dry scrubbers, conventional wet scrubbers and CO₂ packed bed absorbers, making it easier to retrofit in space-constrained power plants. The modular construction enables it to be easily scaled up for larger units. The NeuStream®-S system consumes less water (at around 1.9 L/MW), has zero liquid discharge and has less parasitic power loss (~1.2%) than other conventional FGD systems. It uses about half as much water and parasitic power as spray dry scrubbers, and less than a third of the parasitic power and about a quarter of the water usage of conventional wet scrubbers (Fredell and others, 2012). The use of gas-liquid heat exchangers (see Figure 3) helps lower water consumption, and prevent visible plume formation at the water-cooled stack exit. Dual-alkali systems do not normally suffer from scaling or corrosion problems. If ozone injection is included (NeuStream®-N), then parasitic power consumption will increase due to the power consumption of the on-site ozone generators (see Chapter 6).

Figure 3  NeuStream®-S flowsheet (oxidised mode) (Neumann Systems Group, 2013a)
Capital costs for a NeuStream®-S system are about 50% less than spray dry scrubbers, and operating costs are around 40% less (Fredell and others, 2012). It was estimated that the capital cost of a NeuStream®-S system for a 500 MW plant would be US$179.2 million with annual operating costs of US$27.7 million. Equivalent costs for conventional wet scrubbers are US$394.4 million and US$54.3 million, respectively (Kladder, 2010). This gives savings of ~55% in capital costs and ~50% in operating costs for NeuStream®-S over conventional wet scrubbers. Saleable by-products, such as gypsum, can be produced. Otherwise the filter cake is sent for landfill. Since the scrubber is installed after the ESP or fabric filter, the recovered fly ash can potentially be sold.

A piperazine NeuStream®-C system on a 550 MW (net) subcritical coal-fired power plant will consume 29.7% parasitic power (including steam and compression work) when capturing and compressing 90% of CO₂, and producing a CO₂ product purity of >95%. It would cost US$31 to capture 1 t of CO₂, compared to 61 $/tCO₂ for a standard amine absorber system (Econamine FG Plus™). The CO₂ can be sold for enhanced oil recovery. The smaller footprint of Neutream®-C significantly lowers capital costs, and the use of flash tanks for sorbent regeneration instead of stripper towers also saves on the capital costs. It is claimed that when carbon emission regulations and the implementation of potential carbon tax avoidance are factored into the economics, the sale of CO₂ would be a profitable endeavour for power plant owners (Awtrey and Klein, 2013). The NeuStream® technology has yet to be proved at a full-size unit. More information about the technology can be found on the [www.neumannsystemsgroup.com](http://www.neumannsystemsgroup.com) website.

### 2.4 SkyMine® process

The SkyMine® process, developed by Skyonic Corporation, removes CO₂, SOx, NO₂, mercury and other heavy metals from flue gas by scrubbing with sodium hydroxide, which is electrochemically produced from brine. Saleable by-products, including carbonates and/or bicarbonates, hydrogen and chlorine, are produced. A feature of the process is that it captures the CO₂ as a stable solid (sodium bicarbonate, also known as baking soda). The SkyMine® process can be run in a non-carbon mode, called SkyScraper™, that scrubs just the SO₂, NO₂ and heavy metals from flue gas. In this mode, no carbonate and bicarbonate by-products are produced. A pilot-scale demonstration of SkyMine® at the Luminant Big Brown power plant at Fairfield, TX, USA, in 2007 removed over 99% of SOx and NO₂, 90% of mercury, and 80–90% of CO₂, when burning lignite and subbituminous coal (St Angelo, 2009; St Angelo and others, 2008). A commercial-scale demonstration of the technology, capturing 75,000 tCO₂/y, at Capitol Aggregates’ cement plant in San Antonio, TX, USA, is under construction and scheduled to reach full production in late 2014.

The SkyMine® process can be divided into three main operations: flue gas conditioning, absorption, and electrochemical production. In the flue gas handling stage (see Figure 4), flue gas exiting the ESP or fabric filter is passed through heat exchangers to cool and condense out the moisture. The condensed water is treated and filtered through activated carbon to remove mercury, other heavy metals and particulates, before it is reused elsewhere in the process. The cooled (~30–40ºC) flue gas passes through two absorption columns in series (absorption stage), where it is scrubbed with sodium hydroxide to remove CO₂, SOx, NOx and other acid gases. SOx and NOx react with the sodium hydroxide to form sodium sulphates and nitrates, respectively. CO₂ reacts with sodium hydroxide to form sodium carbonate and bicarbonate. The clean flue gas is then emitted to the atmosphere through the exhaust stack. The process is optimised at Capitol Aggregates’ cement plant demonstration to produce principally sodium bicarbonate (Jones and others, 2011).

The sodium hydroxide reagent is made by electrochemical production (chlor-alkali plant). Brine is first generated by dissolving salt (NaCl) in water, purified and then electrolysed in a low voltage membrane cell to produce sodium hydroxide, hydrogen and chlorine.

The SkyMine® process has a high pollutant removal efficiency, capturing >99% of SOx and NO₂.
>97% of mercury and >90% CO₂ from flue gas (St Angelo, 2009). Around 94% of the CO₂ will be captured at the cement plant demonstration (RDB Environmental Consulting, 2010). Since the CO₂ is captured as solid bicarbonate/carbonate, the environmental concerns associated with CO₂ pipeline transport, groundwater contamination and leakage from underground storage are avoided.

The technology is built primarily from proven commercial systems, and can be retrofitted. The SkyMine®/SkyScraper™ facility can be built next to the power plant and the flue gas piped to it for treatment, eliminating the need for costly remodelling within the power plant. It has been estimated to cost ~US$600 million to install SkyMine® on a 1325 MW coal-fired power plant and would cost ~23 US$/tCO₂ captured, excluding revenue from the sale of by-products (Airlie, 2011). The capital costs of SkyScraper™ are lower than a limestone wet scrubber + SCR system, and has the advantage that no CO₂ is generated during the scrubbing process. SkyMine® is designed to operate at a profit due to the sale of the hydrogen, chlorine and sodium bicarbonate by-products. The ultimate cost of the process will depend on the market demand and price of the saleable by-products. Several chemical revenue streams are possible, depending on choices driven by market conditions, site location and capital investment requirements. For example, the chlorine and hydrogen could be converted into hydrochloric acid, some of which could supply the requirements for HCl use within the chlor-alkali plant and the surplus sold for use in enhanced oil recovery. Or the chlorine could be combined with surplus sodium hydroxide to form sodium hypochlorite (bleach) and sold. The hydrogen could be used in a conventional fuel cell to produce additional electricity, combusted in the coal boiler for supplemental heat, or sold as a commodity gas. Chemical production could occur during off-peak periods when electricity is available at a lower cost (St Angelo and others, 2008). The commercial operation at Capitol Aggregates’ cement plant will produce around 194,600 t of hydrochloric acid, 37,700 t of sodium hypochlorite and 146,400 t of sodium bicarbonate when capturing ~75,000 tCO₂/y (RDB Environmental Consulting, 2010).

Sodium bicarbonate can be used, for example, in algae biofuels production and glass manufacture. If there is no market for the sodium bicarbonate, then it can be safely landfilled, used for mine backfilling or used as a road base. About 2.5 t of sodium bicarbonate is produced for every tonne of coal a plant burns. To capture all carbon emissions from the Big Brown power plant alone, would generate about 13.6 Mt (15 million tons) of sodium bicarbonate. This is nearly ten times the annual worldwide production of sodium bicarbonate (baking soda), according to mining industry estimates (Waco Tribune-Herald, 2008). Thus the market for and revenue from sodium bicarbonate is limited. Transporting the large volumes of sodium bicarbonate away from the plant might make the process uneconomic (depending on the sale of the other by-products and various economic factors). The SkyMine® process can be altered to produce saleable sodium carbonate (used, for example, in glass production) instead of bicarbonate (MacDiarmid, 2013). The on-site production of the sodium hydroxide and saleable products comes at the cost of added complexity compared to some other capture processes.
The SkyMine® process consumes a significant amount of electrical energy, primarily in the production of the sodium hydroxide reagent. It was estimated that the total power requirement for the Capitol Aggregates’ SkyMine® demonstration would be 21.12 MW, of which electrolysis accounts for 18.42 MW (Jones and others, 2011). Total power input can be lowered by using waste heat recovered in the flue gas conditioning step and elsewhere to heat the electrolyte fluids. It is claimed that installing SkyMine® at a 2000 MW power plant would reduce its capacity by 20% to 1600 MW. This compares to a ~40% penalty with carbon capture systems that involve pumping and storing the CO₂ underground (Airlie, 2011). Skyonic Corp is developing a thermolytic process for converting salt into the scrubber reagent to lower energy consumption.

The Capitol Aggregates’ project is estimated to require an additional 860 million L/y of water primarily for cooling purposes, hydrochloric acid production and brining operations (RDB Environmental Consulting, 2010). Water usage is lowered by recovering moisture from the flue gas (conditioning stage) and the wet hydrogen and chlorine gases leaving the electrolysis cell, as well as water recovery elsewhere. The only significant sources of waste material are the wastewater from the brining operation, and the spent activated carbon filter material, which requires disposal by a licensed waste management company, at a cost. More information about SkyMine® can be found on the website http://skyonic.com.

2.5 Comments

The four processes are at different stages of commercialisation. Limestone wet scrubbers have been in commercial operation for years, whilst the Airborne Process™, NeuStream® technology and SkyMine® have yet to be proved on a full-scale coal-fired power plant. NeuStream®-S is currently being installed on a coal-fired power plant, SkyMine® at a cement plant and the Airborne Process™ on plants in China. All the processes have a high SO₂ removal efficiency and, for those designed for the purpose, >90% NOx and mercury removal, and 70–90% CO₂ capture. They all produce saleable by-products, although sales may be limited by proximity to the end market and the availability of cheap transport. A single large power plant can easily overwhelm the by-product market in a fairly large region, and so be unable to sell all of their by-products. This has been the case with gypsum.

Limestone wet scrubbers utilise a limestone slurry as the sorbent, whilst the other three processes use a sodium-based (sodium carbonate or sodium hydroxide solution) sorbent. New sorbents are being investigated. Bench-scale experiments using a urea (a cheap and easily obtained compound in China) and potassium permanganate (KMnO₄) solution, for example, removed over 98% of SO₂, 53% NO and 99% of elemental mercury under optimal conditions (Fang and others, 2013). Sodium humate solution achieved removal efficiencies of over 98% for SO₂ and over 95% for NO₂ under optimal conditions (Hu and others, 2010). A fertiliser by-product is produced with these two newer sorbents.
3 Semi-dry scrubbing processes

Dry scrubbers were developed for desulphurisation of flue gas, but as a co-benefit they also remove some mercury, other heavy metals, and particulates. Dry scrubbers are the second most common FGD system installed on coal-fired power plants, with a share of less than 10% of total installed FGD capacity worldwide. Wet FGD scrubbing is by far the predominant technology, accounting for over 80%.

There are two principal types of dry scrubbers in use today:
- spray dry scrubbers (SDSs);
- circulating dry scrubbers (CDSs).

Both of these systems utilise a calcium-based reagent (calcium hydroxide) which is introduced as a slurry in SDSs and in some CDS designs, as a dry powder with separate injection of water. All of the water introduced into the SDS/CDS vessel is evaporated. So although they are termed dry scrubbers, they do, in fact, consume water and are better classified as semi-dry systems. The dry scrubbers are normally installed after the air heater. After passing through the scrubber, the dry fly ash, reaction products and unused sorbent are collected in a fabric filter or ESP. The use of fabric filters as the particulate collector offers an advantage over ESPs as absorption of additional SO₂, SO₃ and other pollutants occurs in the dust filter cake. The humidity of the flue gas exiting the system favourably affects the performance of ESPs helping to counter the adverse effects of calcium-based sorbents on fly ash resistivity (Ahman and others, 2002).

In Europe, the fly ash is often removed before the flue gas enters the dry scrubber system, unlike most installations in the USA. This enables the fly ash to be sold, and reduces the amount of waste for disposal. Fly ash pre-collection, though, increases capital and O&M costs. It may also lead to a slightly higher sorbent feed rate to compensate for the absence of the calcium oxide component in the fly ash. The fly ash calcium oxide is converted to calcium hydroxide in the reactor, increasing the reactant concentration. The mercury capture benefit from the carbon in the fly ash is also reduced. Injecting a mercury sorbent into the dry scrubber may be necessary to improve mercury capture efficiency, at a cost.

Instead of injecting a calcium-based reagent, the ClearGas™ dry scrubber (see www.clearstack.com) injects aqueous potassium hydroxide (KOH) through dual fluid nozzles into a dry scrubber or duct for combined SOx and NOx removal. The resultant potassium sulphates and nitrates are captured along with the fly ash in a downstream ESP, and can be used as a fertiliser. The technology was developed for coal-fired stokers, and can be used as a polishing unit on coal-fired power plants.

3.1 Spray dry scrubbers

Spray dry scrubbers (SDSs), also called spray dry absorbers or lime spray dryers, were developed in the late 1970s. Today there is around 40,000 MW of capacity worldwide equipped with SDSs, the majority of which (about 95 units) are installed in the USA (Jones and Weilert, 2011). They are most often used on small- to medium-sized (~450 MW) units burning low to medium sulphur (2% S) coals (Moss, 2010). Removal efficiencies are typically in the range 90–98% for SO₂, depending on the sulphur content of coal, over 95% for SO₃, HCl, HF, heavy metals and particulates (PM₂.₅ and PM₁₀), and 0–95% for mercury (dependent on the chlorine content of coal and other factors), with downstream fabric filters (Babcock & Wilcox, 2009; Moretti and Jones, 2012).

In the SDS process (see Figure 5), a concentrated lime slurry (produced from hydrated or quick lime) is introduced into the top of the absorber vessel through rotary atomisers or dual fuel nozzles. These atomise the slurry creating a fine mist of droplets containing the reagent, which reacts with SO₂ and...
SO\textsubscript{3} in the downward flowing flue gas to form calcium sulphite and sulphate. Both elemental and oxidised mercury are adsorbed on the fly ash, calcium sulphite and calcium sulphate particles. The flue gas then passes through the particulate collector before being emitted through the stack. The dry waste products are collected from the bottom of the scrubber and the rest from the particulate collector. A portion of these solids or, more usually, a portion just from the particulate collector, is typically mixed with wastewater and recycled back to the scrubber to improve sorbent utilisation, as well as promoting droplet drying in the SDS vessel. If the fly ash is not removed from the flue gas before it enters the absorber, then recycling alkaline fly ash in the products will remove additional SO\textsubscript{2} and SO\textsubscript{3}.

Some scrubber designs utilising rotary atomisers introduce the flue gas through a central roof gas disperser, whilst another (Alstom) incorporates three roof mounted gas dispersers for use on units up to a 450 MW capacity (Buschmann, 2008). For large utility boilers (450 MW), the GEA Niro SDS introduces the flue gas through two locations, a roof mounted gas disperser and a central gas disperser. The gas dispersers are designed to distribute the flue gas evenly around the atomiser(s) units at the required velocity to maximise contact between the flue gas and droplets. Scrubbers with dual fuel nozzles introduce the flue gas through an array of these nozzles installed on the roof. Careful control of the gas distribution, slurry flow rate and droplet size ensure that the droplets fully evaporate before contacting the internal walls of the scrubber. The water must evaporate sufficiently to avoid formation of undesirable deposits and corrosion problems.

SO\textsubscript{2} removal efficiencies are typically in the range 90–95%, although some plants can remove 98% with an integral fabric filter (Babcock & Wilcox, 2009; Moretti and Jones, 2012). Ca:S stoichiometric ratios for a 0.6% sulphur subbituminous coal, 1.3% sulphur bituminous coal and 2% sulphur bituminous coal are typically 1.2, 1.4 and 1.6, respectively, for a 95% SO\textsubscript{2} removal efficiency (Sargent & Lundy, 2007). The SO\textsubscript{2} removal efficiency is influenced by the coal sulphur content (SO\textsubscript{2} inlet concentration), inlet temperature, flue gas humidity, slurry droplet size and other factors. The amount of alkaline material that can be added to the SDS vessel is limited by the amount of water that can be supplied to the flue gas, and the weight percentage of suspended solids in the lime slurry that can be successfully fed to the atomisers. The amount of water that can be added is a function of the flue gas inlet temperature and the SDS outlet temperature (degrees above the adiabatic saturation temperature). As the coal sulphur content increases, the amount of lime that must be added increases rapidly as both the inlet SO\textsubscript{2} concentration and the required percentage removal increase. A point is reached where further increases in the coal sulphur content or SO\textsubscript{2} removal performance achieved are not possible due to the inability to add more lime. Similarly, the amount of material that can be recycled from the particulate control device is also limited by the amount of water that can be added. This can restrict both SO\textsubscript{2} removal efficiency and overall reagent utilisation (Baker and others, 2012).
Since most of the SO\textsubscript{2} capture occurs when the sorbent is still moist, adding deliquescent salts, such as chlorides, can improve SO\textsubscript{2} removal efficiency by extending the time in which the sorbent remains moist. A similar effect is achieved when coals with elevated chloride content are used (Srivastava and Jozewicz, 2001). Chlorine in the flue gas reacts with the calcium sorbent to form calcium chloride which is a deliquescent salt. However, the salts can form unwanted deposits on the scrubber walls and downstream equipment. Therefore the addition of deliquescent salts must be carefully controlled.

SDSs were not designed for mercury removal but, as a co-benefit, they can remove around 0–95\% of the mercury. The removal efficiency is dependent on a number of factors, including the mercury content of coal, the chlorine and sulphur coal contents and their resultant interactions with mercury, the unburnt carbon content of fly ash, the mercury species present in the flue gas, and the flue gas temperature. High chlorine coals (producing 500 to 2000 ppm Cl in the flue gas) have a higher removal efficiency than low chlorine coals (Trovant, 2013), due to the increased conversion of elemental mercury (Hg\textsubscript{0}) to the more easily absorbed oxidised mercury (Hg\textsuperscript{2+}). Mercury removal efficiency can be >95\% for US high chloride bituminous coals, but only around 25\% for low chlorine subbituminous coals (Sloss, 2008). Higher sulphur coals that produce more SO\textsubscript{2} in the flue gas do not directly affect mercury speciation but can interfere with the potential of other components, including chlorine, to oxidise mercury (Trovant, 2013). Fly ash with a high unburnt carbon content enhances mercury capture by adsorbing oxidised mercury, where it becomes particulate-bound mercury and is subsequently captured in the fabric filter or ESP. While the fly ash unburnt carbon content is a function of several boiler operational variables, bituminous coals generally produce higher unburnt carbon than subbituminous coals, which in turn produce higher levels than lignite (Trovant, 2013). The mercury capture efficiency is higher with fabric filters than ESPs due to continuing reactions in the filter cake. Most of the particulate-bound mercury (Hg\textsuperscript{0}) is captured in the particulate control device.

Injecting mercury sorbents into the ductwork upstream of or into the SDS vessel can increase mercury removal efficiency, and is necessary for low chlorine subbituminous coal and lignite in order to meet mercury emission limits. Brominated activated carbons are popular as bromine has a far greater oxidation effect on mercury than chlorine. The injection of brominated activated carbon upstream of the SDS was tested for about 7 weeks at the 350 MW Comanche Unit 1 in Pueblo, CO, USA, firing subbituminous (PRB) coal. Mercury emissions were reduced to below the required 0.07 kg/GWh (0.15 lb/GWh). Average emissions during the 4.49 mg/m\textsuperscript{3} (0.28 lb/m\textsuperscript{3}acft) and 7.69 mg/m\textsuperscript{3} (0.46 lb/m\textsuperscript{3}acft) injection tests were between 0.0018 and 0.0023 kg/GWh (0.004–0.005 lb/GWh); average baseline mercury emissions (before sorbent injection) was 0.012 kg/GWh (0.027 lb/GWh). The cost of compliance for the plant using this approach was estimated at somewhere between US$200,000 and US$1million, assuming a brominated activated carbon cost of 2.3 US$/kg (1.05 US$/lb), and a factor of 2–3 uncertainty in the actual feed rate (Magno and others, 2011). Injecting brominated activated carbon upstream of the SDS at the Hocomb and Laramie River power plants in the USA, both of which burn PRB coal, reduced mercury emissions by over 90\% (Durham and others, 2005). Non-halogen and non-carbon mercury sorbents, such as liquid MerControl 6012, are commercially available for injecting into the SDS to control mercury (Smokey and others, 2012). Chemical compounds are also available that can be added to the coal prior to combustion or injected into the furnace that increase the oxidised mercury fraction in the flue gas, which is then captured in the SDS.

SDS systems are considered to be efficient and reliable. Auxiliary power consumption is around 0.5–1\% compared to 1–1.5\% for wet scrubbers (European Commission, 2006). Water consumption is ~20–40 L/1000 m\textsuperscript{3} of flue gas (European Commission, 2006) or ~0.14 L/kWh (Singleton, 2010), due primarily to the preparation of the hydrated lime slurry. Water usage is a function of the temperature of the flue gas and its flow rate, and is about 60–70\% lower than limestone wet scrubbers (Carpenter, 2012). No wastewater is produced since all the water is evaporated in the SDS vessel. The solid products are dry and easily handled. Unless the fly ash is pre-collected, it cannot be sold. The solid wastes are generally landfilled, which can be expensive. Potential applications include waste stabilisation, road construction, landscaping and mine backfilling. More research is needed on ways to utilise the waste products.
SDSs can typically operate at loads ranging from ~25% to 100% (Jones and Weilert, 2011), although some manufacturers have claimed a turndown to 10% load (Buschmann, 2008). The ability of SDSs to operate at lower loads is dependent on the flue gas temperature entering the scrubber. No reagent can be fed unless the flue gas is hot enough to dry the slurry droplets to a powder before the flue gas exits the scrubber. This therefore hampers the ability of SDSs to control emissions at low loads and prolongs the time during start-up before SO2 removal can begin. The reagent feed system can rapidly change the amount of sorbent being fed into the scrubber and so can respond to load changes, once the system is operating (Jones and Weilert, 2011). None the less, injecting dry hydrated lime into the bottom of the SDS vessel allows the downstream fabric filter to be coated with alkaline material prior to the first coal feed and normal SDS start-up sequence. This reduces SO2 emissions on a cold boiler start-up. Tests at the 110 MW (gross) Unit 5, near Gillette, WY, USA, where PRB coal is fired, reduced SO2 emissions by 50–65% compared to a unit start-up without dry hydrated lime injection. Injecting ~2720–4080 kg of dry hydrated lime into the flue gas at the air heater outlet before coal firing, lowered SO2 emissions by about 50–67%. Both methods enabled the unit to meet SO2 emission limits during boiler start-up. Tests at a power plant in the Czech Republic showed that injecting dry hydrated lime into the SDS vessel can also improve SO2 removal performance during normal operation (Jankura and others, 2012).

A SDS is cheaper to install than a wet scrubber for small- to medium-size units (European Commission, 2006), but its capital cost advantage may not apply for large power plants when multiple SDS units are required. The capital cost for retrofitting a SDS system on the Big Stone Unit 1 (475 MW net) was estimated to be US$141,300,000 (US$2009), or a unit cost of 297 US$/kW, compared to US$171,800,000 or 362 US$/kW for a limestone wet scrubber (Otter Tail Power, 2009). The costs were calculated for a 90% removal efficiency for the SDS compared to 95% for the wet scrubbers. But SDSs are generally more expensive to operate due to their slightly lower sorbent utilisation (when achieving comparable SO2 removal), higher sorbent costs and the costs of waste disposal. SDSs cost about the same to install as circulating dry scrubbers (Jones and Weilert, 2011), but their O&M costs can be higher due to the wear and erosion of the slurry atomisers and of the equipment used in the preparation, handling and transport of the slurries (Buecker and Hovey, 2013). SDSs with fabric filters can capture more SO3, HCl, HF and mercury than limestone wet scrubbers, and with their smaller footprint, may be preferred for retrofit applications.

### 3.2 Circulating dry scrubbers

The circulating dry scrubber (CDS) technology was first developed in Germany in the 1980s. Today, the total capacity of utility units worldwide using this technology is over 15,000 MW (Jones and Weilert, 2011), with units in Europe, Asia (particularly China), and the USA. CDS systems can remove 90–>98% of SO2 (depending on the sulphur content of coal), >99% of SO3, HCl, HF and particulates (PM_{2.5} and PM_{10}), and up to 95% of mercury (dependent on the coal’s chlorine content) with fabric filters (Ake and others, 2012; Giglio and Graf, 2012).

Unlike SDSs, CDSs are upflow reactors in which the flue gas and reactants are introduced through the bottom of the absorber. Sulphur dioxide reacts with the humidified hydrated lime (calcium hydroxide) sorbent to form calcium sulphites and sulphates. Oxidised mercury is absorbed on the fly ash and, if injected, by the mercury sorbent. The reaction products, particulate-bound mercury, spent and unreacted sorbent, along with the fly ash, if it is not pre-collected, are removed by the particulate control device and continuously recycled to the scrubber to maximise sorbent utilisation. The cleaned gas is emitted through the stack. A small portion of the reaction by-products are removed to keep a constant inventory of solids in the system. The reactions to remove the gaseous pollutants can either take place in a fluidised bed (circulating fluidised bed scrubbers and gas suspension absorbers) or in an entrainment process (NID™ and EAD™).

**Circulating fluidised bed (CFB) scrubbers** (also termed circulating dry scrubbers) are in operation
on facilities ranging in size from less than 10 MW to 420 MW. Multiple units are required for plants with a higher capacity, although single-unit designs up to 750 MWe are now available (Bönsel and others, 2012).

A flow diagram of the CFB system (Graf-Wulff design) at the Dry Fork station near Gillette, WY, USA, is given in Figure 6. The flue gas enters the bottom of the CFB reactor and flows upwards through a bank of venturis. These increase the velocity of the flue gas before it mixes with the dry hydrated lime and recycled solids to create the characteristic fluidised bed. In some designs, such as the Graf-Wulff (now part of Foster Wheeler) and Turbosorp® (developed by Austrian Energy and Environment), the fresh sorbent and recycled solids are injected above the venturis, whereas other designs, such as the Lurgi Lentjes (now Doosan Lentjes), introduce them below the venturis. The recycled solids are typically transported via air slides to the CFB absorber. Water is sprayed into the fluidised bed to both humidify and cool the flue gas to ~70°C or about 20–25°C above its adiabatic saturation temperature. The water is rapidly dispersed over the surface of the particles in the bed, forming a thin layer of liquid on each particle. The SO₂, SO₃ and other acid gases are absorbed into the liquid layer and react with the Ca(OH)₂.

The fluidised bed recirculates the reactive material within the reactor to achieve a high retention time. An additional benefit is the continuous abrasion of the sorbent particles, resulting in the exposure of fresh reactive surfaces. The flue gas takes ~5 s to pass through a 23 m deep fluidised bed (Moss, 2010). At low boiler loads, when the flue gas flow is low, some of the cleaned flue gas is returned to the CFB absorber in order to maintain sufficient velocity through the venturis to sustain the fluidised bed.

A multi-stage humidification system has been developed by Zhejiang University’s Institute for Thermal Power Engineering whereby the water is injected in multiple stages. This distributes the water more evenly throughout the reaction zone, and the time that the humidity content is above the critical moisture point is extended, increasing the effective residence time for the reactions. SO₂ removal efficiency increased by over 1% when the water was injected in two stages, whilst the total water consumed was the same as that consumed in single stage humidification (Gao and others, 2010). Over 140 systems are in operation on power plants, incinerators and other industrial plants in...
China. The technology is being marketed by Marsulex Environmental Technologies (under licence) in the USA.

The Gas Suspension Absorption (GSA) process was developed in Denmark by FLS Miljø (FLSmidth) and has been in commercial use since the 1980s on over 70 installations in the power generation, waste-to-energy (municipal incinerators), iron and steel, and cement industries. In the power industry, the technology is typically applied to small- to medium-sized boilers burning low to high sulphur coals.

The GSA process is similar to CFB scrubbers but has an integral cyclone for recirculating the solids via a recirculation box to the fluidised bed reactor. The lime sorbent and cooling water are injected via a single dual fluid nozzle installed on the venturi. The sorbent can be quick lime (which is first slaked to produce a 20% solid slurry) or dry hydrated lime (FLSmidth, 2010). Around 99% of the solids (fly ash, lime and reaction products) in the flue gas exiting the reactor are captured in the cyclone and introduced back into the reactor just above the venturi. Activated carbon is injected into the duct between the cyclone outlet and the particulate control device (ESP or fabric filter) to capture mercury.

Alstom’s Novel Integrated Desulphurisation (NID™) technology (previously called Flash Dryer Absorber) has been around for more than 20 years. There are over 100 installations covering applications in the power generation, iron and steel, and waste-to-energy industries (Alstom, 2012), including about 60 coal-fired power plants in Europe, Asia and the USA. This number is increasing as several electric utilities in the USA have recently announced plans to install NID™ systems.

The unique feature of NID™ technology is its J-shaped duct reactor, which has a square cross section, and is integrated with a pulse jet fabric filter or, less commonly, an ESP. Hydrated lime (Ca(OH)₂), quick lime (CaO) or alkaline ashes can be used as the reagent. CaO is dry slaked to Ca(OH)₂ in the system. Unlike CFB scrubbers, fresh reagent and the fly ash, reaction products and unreacted solids collected from the particulate collector are hydrated in the humidifier mixer by the addition of water (see Figure 7). The humidified Ca(OH)₂ mixture is then injected near the bottom of the NID™ absorber into the upward flowing flue gas. With the high solids-to-water ratio, evaporation occurs rapidly, cooling and humidifying the flue gas, whilst flash drying the particulates. No water is sprayed into the absorber, unlike CFB scrubbers. The chemical reactions and drying times within the absorber take less than 2 s.

![Figure 7 NID™ process flow diagram (EPRI, 2007)](image-url)
The fast reaction time in the absorber is possible due to one of the outcomes from the reaction between quick lime and water that generates hydrated lime. The physical and chemical properties of the CaO-water reaction reduce the particle size from over 800 µm to sometimes less than 10 µm. The large surface area created enables the reaction with SO₂ to proceed effectively within a short residence time (Buecker and Hovey, 2013).

The Enhanced All-Dry (EAD™) Scrubber, developed by Procedair (now Solios Environnement) in the 1980s, is a dry circulating entrained process. The flue gas and dry hydrated lime reagent enter the bottom of the vertical venturi tower and pass upwards into the reaction zone before the flue gas is internally redirected back downwards. In March 2012, Hitachi Power Systems America signed a licence agreement with Solios Environnement to design and supply the technology to the global electric utility market. The process has been installed on industrial plants, but has not yet been installed on coal-fired power plants, and so will not be discussed any further.

CFB systems can be applied to power plants burning low to high sulphur coals. A CFB scrubber has recently been installed on the bituminous coal-fired J S Cooper Unit 2, near Burnside, KY, USA, that is designed to remove over 95% of the SO₂ with an inlet loading of ~3096 ppmv SO₂ (7.2 lb SO₂/MMBtu) (Jones and others, 2012). NID™ is applicable to coals with a sulphur content below 4.5% (Johansson, 2012). All of the CDS systems (CFB, GSA and NID™) have a high multi-pollutant capture capability, and can meet the US MATS and the European Industrial Emissions Directive emission limits. They can remove over 98% of SO₂ (depending on the SO₂ inlet concentration), and over 99% of SO₃, HCl, HF and particulates (PM₂.₅ and PM₁₀) (Ake and others, 2012; Giglio and Graf, 2012). Typical stoichiometric ratios of 1.5, 1.8 and 2 are required for 98% SO₂ removal in CFB scrubbers when burning subbituminous (0.6% sulphur), low sulphur (1.3%) bituminous and medium sulphur (2%) bituminous coals, respectively (Sargent & Lundy, 2007).

In some cases, such as when firing high chlorine bituminous coals, up to 95% of mercury has been removed without the injection of activated carbon (Ake and others, 2012). Higher mercury removal is possible by injecting activated carbon or another mercury sorbent. Like SDSs, a mercury sorbent is necessary when firing low chlorine subbituminous coal or lignite. The effectiveness of activated carbon can be limited by either low chlorine or high SO₃ levels in the flue gas. The injection location can be selected to avoid these issues, for example, by injecting ahead of the reactor for low chlorine coals, or in the reactor for high sulphur coals (Ake and others, 2012). An example of the emission reduction levels achieved with the installation of a CFB (Graf-Wulff design) scrubber is given in Table 2 for the Dry Fork power plant. The plant, which fires PRB subbituminous coal, reduced SO₂ by 95–98% to levels below 50–60 mg/m³, opacity was less than 1%, particulate emissions were below 3 ppm, and over 95% of mercury was removed (activated carbon was also injected) to levels below 2.35 µg/m³ (20 lb/TWh) (Bönsel and others, 2012; Giglio and Graf, 2012). No CO₂ is generated in the desulphurisation reactions to add to the CO₂ emissions from the power plant (unlike limestone wet scrubbers).

The VersaMAPSTM system (see www.boldeco.com), developed by BoldEco Environment, additionally removes NOₓ by installing a low temperature oxidiser reactor ahead of the CFB scrubbers (EcoSorb™). The proprietary reagent (an oxidising reagent combined with an activator) is injected into the oxidiser, converting NO to NO₂, and then ultimately to nitric acid, which is neutralised in the CFB reactors. The oxidising reagent also aids mercury capture by oxidising elemental mercury into mercury oxide that is removed downstream. The system uses multiple, parallel CFB scrubbers, close coupled to high efficiency fabric filters. It has been installed on waste incinerators and other industrial plants, but has not yet been applied to a coal-fired power plant.

Adding lime and water separately in CFB scrubbers means that the lime feed can be easily adjusted to handle variable SO₂ concentrations during start-up, from load changes or if flexibility is needed in fuel selection. This differs from a SDS, which cannot feed any reagent unless the flue gas is hot enough to dry the slurry droplets to a powder before the flue gas exits the spray dryer. However, dry
hydrated lime can be injected into SDSs before start-up to reduce SO₂ emissions (see Section 3.1). The injection water for CFB scrubbers and the NID™ humidifier mixer does not have to be of high quality since it evaporates during the process (Alstom, 2012; Buecker and Hovey, 2013). The Deerhaven power plant near Gainesville, FL, USA, uses water from the ash pond in its CFB scrubber (Ake and others, 2010). Utilising low quality water, such as cooling tower blowdown, could potentially lower the overall amount of wastewater to be treated and reduce water pollution from the power plant. SDSs require higher quality water for lime hydration so that excessive amounts of sulphates or bicarbonates do not react with the lime.

Just enough water is introduced into the gas stream in CDSs to lower its temperature to the optimum level for the reactions to occur, but no more than can be fully evaporated; over wetting the particles can cause scaling problems in the reactor. Therefore no wastewater is generated. The by-products are dry and so are easily handled. They can be disposed of in a landfill or potentially used in construction, mine backfilling, landscaping or other applications. The by-products from the Dry Fork CFB scrubber are being utilised for land reclamation at the nearby open-cast coal mine (Giglio and Graf, 2012).

CDSs are considered to be efficient and reliable, and do not normally suffer from scaling, plugging or corrosion problems. CFB scrubbers have good turndown capability to below 30% maximum continuous rating with a clean flue gas recirculation loop and to around 50% without flue gas recirculation (Bleckinger and others, 2012; Jones and others, 2012). One feature of NID™ is its modular design, where each module has its own reactor and integrated fabric filter, and can handle the equivalent of ~75 MW of flue gas. The modular design enables flexible unit turndown in that individual modules can be taken out of service until only one remains in service. The final module can be turned down to 50% (without flue gas recirculation) for very low load operation (Buecker and Hovey, 2013).

### Table 2  Dry Fork power plant flue gas properties and emission reductions (Bönsel and others, 2012; Giglio and Graf, 2012)

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>Inlet design</th>
<th>Outlet design</th>
<th>Outlet measured</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flue gas flow</strong></td>
<td>m³/h</td>
<td>3,045,000</td>
<td>2,630,000</td>
<td>2,700,000</td>
</tr>
<tr>
<td></td>
<td>acfm</td>
<td>1,792,000</td>
<td>1,550,000</td>
<td>1,590,000</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>°C/°F</td>
<td>146/294</td>
<td>70–80/155–175</td>
<td>80–95/175–205</td>
</tr>
<tr>
<td><strong>SO₂</strong></td>
<td>mg/m³</td>
<td>800–2200</td>
<td>60–75</td>
<td>15–50</td>
</tr>
<tr>
<td></td>
<td>lb/10⁶ Btu</td>
<td>0.66–1.79</td>
<td>0.06</td>
<td>0.01–0.04</td>
</tr>
<tr>
<td></td>
<td>ppmv</td>
<td>280–770</td>
<td>20–25</td>
<td>5–17</td>
</tr>
<tr>
<td><strong>SO₃</strong></td>
<td>mg/m³</td>
<td>25–42</td>
<td>1–2</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>ppmv</td>
<td>8–14</td>
<td>0.3–0.6</td>
<td>–</td>
</tr>
<tr>
<td><strong>HCl</strong></td>
<td>mg/m³</td>
<td>8–15</td>
<td>4–6</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>ppmv</td>
<td>5–9</td>
<td>2–3</td>
<td>–</td>
</tr>
<tr>
<td><strong>Particulates</strong></td>
<td>mg/m³</td>
<td>4000–6000</td>
<td>14–20</td>
<td>2–4</td>
</tr>
<tr>
<td></td>
<td>lb/10⁶ Btu</td>
<td>3–5</td>
<td>0.012</td>
<td>0.002</td>
</tr>
<tr>
<td><strong>Hg</strong></td>
<td>%</td>
<td>–</td>
<td>–</td>
<td>50–70 (without activated carbon injection)</td>
</tr>
<tr>
<td><strong>Opacity</strong></td>
<td>%</td>
<td>–</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>
CFB scrubbers consume ~0.3–1% of the electric capacity of the plant (European Commission, 2006), largely from the booster ID fans needed because of the pressure drop caused by the reactor. However, Chenevey and Smith (2011) estimated that a 205 MWe station with a CFB scrubber system would consume ~2% of the power and ~833 L/min of water when removing >98% of the SO₂ (inlet SO₂ concentration is 1400 ppm or 3.2 lb/MMBtu). Maintenance would cost 15 US$/kW. Parasitic power consumption of NID™ is ~0.7% (Johansson, 2012). CDSs consume ~60–70% less water than limestone wet scrubbers (Carpenter, 2012).

CDS systems are easy to maintain as they do not require high maintenance mechanical equipment, such as grinding mills and abrasion resistant slurry pumps, and no wastewater treatment facility is needed. The waste products are dry and so easily handled. Consequently, CDSs have lower capital and maintenance costs and require a smaller footprint than limestone wet scrubbers. Capital costs for a NID™ system are 30% lower than a comparable limestone wet scrubber (Johansson, 2012). The capital cost of the CFB scrubber (Turbosorp®) installation at the 105 MW Greenidge Unit 4 was 229 US$/kW ($2005). This includes the cost of a lime hydrator system. If included, an activated carbon injection system would add about 6 US$/kW to the capital costs. Fixed and variable O&M costs are around 6.50 US$/kW (Connell and others, 2008). The CFB scrubber’s footprint at the Dry Fork station is about 20–30% of that of a comparable wet scrubber and 70–80% of a comparable SDS (Bönsel and others, 2012). The footprint of a NID™ module is less than 50% of a comparable CFB scrubber or SDS (Alstom, 2012), making it suitable for retrofit applications where space is more limited. However, CDSs are more expensive to operate than limestone wet scrubbers due to their consumption of a more expensive reagent. Hydrated lime can be purchased or less expensive quicklime (CaO) bought and hydrated on-site. Furthermore, CDSs generate solid wastes that have little marketable value and require landfilling, which can be expensive.

3.3 Comments

The SDS and CDS technologies are compared in Table 3. The pollutant removal rates are maximum removal efficiencies and will be site specific since they are partly dependent on coal properties, such as sulphur and chlorine contents, and operational factors. Since these flue gas treatment systems are not primarily designed to reduce mercury emissions, the amount of mercury captured is variable. The systems can be adjusted to enhance mercury capture, for example, by lowering temperatures in the flue gas and ESP systems, or increasing unburnt carbon to enhance mercury capture in fabric filters. But these adjustments could cause detrimental effects elsewhere. Otherwise a mercury sorbent can be injected upstream of or into the absorber. Although CO₂ is not emitted in the desulphurisation process (unlike limestone wet scrubbers), it is emitted from on-site lime kilns (if present) where limestone is calcined to produce calcium oxide.

A significant difference between the two technologies is how the reagent is added to the absorbers. In SDSs, fresh lime reagent and recycled solids are added as a finely atomised slurry, whereas CFB scrubbers add the fresh reagent and recycled solids as a dry powder and inject water separately. This enables the CFB scrubbers to treat flue gas from higher sulphur coals and to achieve a higher SO₂ removal efficiency.

There appears to be little difference between the installed capital costs of SDS and CDS systems (Jones and Weilert, 2011; Sargent & Lundy, 2007). Although the fabric filter for a CDS system will be larger and must be elevated, this additional cost is offset by the costs of the larger SDS absorber and the equipment associated with the slurry recycle system. Operating costs due to reagent usage will be higher for CDS systems. An analysis by Jones and Weilert (2011) indicated that CDS technology requires 20% more reagent than SDSs at the same conditions. This increased reagent usage translates into a greater production of waste material to be landfilled. The difference in power consumption between the two technologies is not significant. Even though a CDS system has a higher pressure drop, and hence higher fan power, this is offset by its lack of large atomiser drive motors and auxiliary
A CDS system generally requires a smaller number of motors than a SDS system. An electric utility in the USA that is operating CFB scrubbers alongside units with SDSs have reported lower O&M costs with the CFB scrubbers (Morris, 2010).

Research is being conducted on sorbents for CFB scrubbers that can be utilised without the need for flue gas humidification. Sorbents that consist of fine calcium-containing particles adhering to the surface of larger ash particles have been developed by researchers at Tsinghua University in China.

### Table 3  Comparison of SDS and CDS technologies (Ake and others, 2012; European Commission, 2006; Giglio and Graf, 2012; Jones and Weilert, 2011; Moretti and Jones, 2012)

<table>
<thead>
<tr>
<th></th>
<th>SDS system</th>
<th>CDS system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber configuration</td>
<td>downflow reactor</td>
<td>upflow reactor</td>
</tr>
<tr>
<td>Sorbent</td>
<td>Ca(OH)(_2) slurry prepared from slaked lime or hydrated lime fed into reactor via an atomiser</td>
<td>CFB – dry hydrated lime (Ca(OH)(_2)) directly injected into reactor through venturis&lt;br&gt;NID™ – humidified Ca(OH)(_2)</td>
</tr>
<tr>
<td>Water feed method</td>
<td>water included in slurry reagent</td>
<td>CFB – direct injection into reactor&lt;br&gt;NID™ – water included with humidified sorbent</td>
</tr>
<tr>
<td>Recycle method</td>
<td>prepared as a slurry and fed via atomiser into reactor</td>
<td>CFB – air slide for dry feed into reactor&lt;br&gt;NID™ – mixed with sorbent and injected into reactor</td>
</tr>
<tr>
<td>Absorber size, MW equivalent of flue gas</td>
<td>up to 450</td>
<td>CFB – up to 750&lt;br&gt;NID™ – ~75</td>
</tr>
<tr>
<td>SO(_2) removal, %</td>
<td>90–98</td>
<td>&gt;98</td>
</tr>
<tr>
<td>SO(_3), HCl, HF removal, %</td>
<td>95–98+</td>
<td>95–99</td>
</tr>
<tr>
<td>Hg removal, % (may incorporate a mercury sorbent)</td>
<td>&gt;95%</td>
<td>&gt;95%</td>
</tr>
<tr>
<td>Fuel flexibility</td>
<td>low to medium (2%) sulphur coals</td>
<td>low to high sulphur coals</td>
</tr>
<tr>
<td>Sorbent products (dry)</td>
<td>CaSO(_3), CaSO(_4), CaCl(_2) and fly ash</td>
<td>CaSO(_3), CaSO(_4), CaCl(_2) and fly ash</td>
</tr>
<tr>
<td>Residence time, s</td>
<td>2–15</td>
<td>CFB – 2–6&lt;br&gt;NID™ – 2</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>lower than CDS</td>
<td>CFB – ~10 cm water column more than SDS</td>
</tr>
<tr>
<td>Parasitic power consumption, %</td>
<td>0.5–1</td>
<td>0.3–1</td>
</tr>
<tr>
<td>Water consumption</td>
<td>similar to CDS</td>
<td>similar to SDS</td>
</tr>
<tr>
<td>Reagent consumption</td>
<td>lower than CFB (with recycle)</td>
<td>CFB – up to 20% higher than SDS at same conditions</td>
</tr>
<tr>
<td>Waste disposal</td>
<td>less than CFB</td>
<td>CFB – up to 15% more waste products than SDS</td>
</tr>
<tr>
<td>SO(_2) removal capability during start-up and at low load</td>
<td>limited due to water injected with the slurry reagent</td>
<td>CFB – greater than SDS due to independent injection of water and reagent</td>
</tr>
<tr>
<td>Load following ability</td>
<td>no significant difference</td>
<td>no significant difference</td>
</tr>
</tbody>
</table>
They are prepared by rapidly hydrating lime (CaO) with coal fly ash, CFB boiler ash or boiler ash, and then drying and crushing the product. Desulphurisation efficiencies of 67–83% were achieved in a pilot-scale CFB scrubber system at a Ca:S ratio of 2 and bed temperatures of 600–800ºC. The desulphurisation efficiency was increased to 95% at a bed temperature of 750ºC and Ca:S ratio of 1.5 by reusing the spent sorbent. The amount of CaSO₄ in the by-product means it could be used to treat alkali soils (Li and others, 2011; Zhang and others, 2006).

Sorbents that can lower both NOx and SOx emissions are being developed. This can be achieved by oxidising NO, the chief component of NOx, into NO₂, which is water-soluble. Oxidants, such as sodium chlorite, permanganate and ozone, have been investigated. For example, removal efficiencies of ~96% for SO₂ and ~73% for NO have been achieved in CFB scrubbers when using a multi-composite sorbent prepared from liquid sodium chlorite (NaClO₂) and sodium hypochlorite (NaClO), along with solid slaked lime (Zhao and others, 2012). The VersaMAPSTM system (see Section 3.2) incorporates a low temperature NO oxidiser reactor ahead of the CFB scrubbers. But the technology has only been applied to small-scale boiler plant. Unfortunately, energy consumption of the ozone generator can be high, and sodium chlorite and permanganate produce by-products can adversely affect the environment, and their costs can be high. Spraying humidified water containing potassium ferrate (K₂FeO₄) into a CFB scrubber, with dry slaked lime, could avoid these problems. Removal efficiencies of 96% for SO₂ and 67% for NO were obtained in bench-scale tests with a ferrate concentration of 0.03 M, and an inlet flue gas temperature of 130ºC, residence time of 2.2 s, and a molar Ca/(S+N) ratio of 1.2. The by-products are environmentally benign (Zhao and others, 2011b).
4 Dry technologies

This chapter discusses dry multi-pollutant systems where essentially no water is consumed in the process. It begins with two regenerable systems, namely ReACT™ and SNOX™, before discussing catalytic filter systems and technologies that combine sorbent injection with a particulate control device (Max-9™ and TOXECON™ technologies).

4.1 Activated carbon/coke processes

The activated carbon or coke process is a dry, regenerable system that simultaneously removes SO₂, SO₃, NOx, mercury, HCl, HF and particulates. Coal-fired power plants usually use activated coke as the sorbent. Although its surface area is less than conventional activated carbon, it is cheaper to produce. The flue gas is passed through a moving bed of activated coke to remove SOx and ammonia is injected for NOx removal. The sorbent is regenerated in a separate vessel.

The activated coke process was developed by Bergbau Forschung (now Deutsche Montan Technologie GmbH) in Germany, and further developed in Japan and elsewhere. The planned coal-fired power plant in Hami City, China (two supercritical 660 MW units) will employ an advanced activated coke process for desulphurisation (ResearchViews, 2011). The following section discusses the commercial ReACT™ process. A similar process is being developed by the Beijing Research Institute of Coal Chemistry in China in which the ammonia is injected directly into the activated carbon vessel. A large-scale demonstration of the system is planned before 2015 (Chen and Liu, 2011).

4.1.1 ReACT™ process

The dry ReACT™ (Regenerative Activated Coke Technology) process is marketed by J-POWER EnTech in Japan (see www.jp-co.co.jp/entech_e/index.html for more details). It has been installed on coal-fired power plants in Japan (Takehara (350 MW fluidised bed combustion unit) and Isogo (two 600 MW units)) and Germany, on sintering plants, incinerators and other industrial plants. Wisconsin Public Services is installing a ReACT™ system at its Weston Unit 3 at an estimated total cost of US$275 million, the first commercial application in the USA (FGD & DeNOx Newsletter, 2013). Over 99% of SO₂ and SO₃, 20–80% NOₓ, >90% of mercury (both elemental and oxidised) and ~50% of the particulates are removed in the process when burning low to medium sulphur coals (Peters, 2011). The ReACT™ system is installed after the particulate control device and so ReACT™ acts as a polishing stage for particulates.

The process involves three stages, namely adsorption, regeneration and by-product recovery (see Figure 8). In the adsorption stage, ammonia is injected into the flue gas which then passes horizontally through the absorber (a single- or two-stage tower) containing a moving bed of coal-derived activated coke. The activated coke flows slowly downwards through a series of modules installed side by side. SO₂, SO₃, NOx and mercury are removed through adsorption, chemisorption and catalytic reactions. SO₂ reacts with oxygen and water vapour in the flue gas (through catalytic oxidation) to form sulphuric acid, which is adsorbed on the activated coke. It additionally reacts with ammonia to form ammonium sulphate and bisulphate. SO₃ reacts with water vapour, also forming sulphuric acid. NOx is catalytically reduced on the activated coke surface, reacting with ammonia to form nitrogen and water. Mercury is retained on the activated coke. Particulates are removed by their impact on the coke pellets. The clean flue gas exits the adsorber and is released through the stack. The activated coke takes ~80–120 h to pass through the adsorber and the residence time for the flue gas is ~10 s.
The spent sorbent is conveyed via a bucket elevator to the top of the regenerator where it falls down through three indirect heat exchanger sections where, in turn, it is pre-heated to ~200°C, heated to 400–500°C, and cooled to 150°C or lower. The reduction of NOx to N2 is completed. The adsorbed sulphuric acid and ammonium compounds in the activated coke decompose to SO2, N2 and water in the heated zone, and the mercury is desorbed. The desorbed gases flow upwards and the mercury is re-adsorbed by the activated coke. Mercury is removed with the activated coke during planned outages every few years. This occurs every 2–3 y at the Isogo power plant in Japan, when 90 t (or <0.09 t/MW/y) of used activated coke is removed. After cooling, the regenerated activated coke is screened to remove fines and captured fly ash before it is returned to the adsorber. It should be noted that activation of the activated coke increases with time because the surface area of the activated coke increases during the recycling process.

Ammonia can be injected into the regenerator to enhance NOx removal and maximise activated coke utilisation. It generates more reducing compounds on the surface of the activated coke, which increases NOx removal efficiency. This allows optimisation of the system performance and cost based on the trade-off between the cost of ammonia and activated coke, which both reduce NOx emissions. The optimum design and operating point is site-specific and depends on the prices of ammonia and activated coke (Washington Group International, 2005).

The SO2-rich gas (SO2, N2, CO2 and water) exits the regenerator and passes to the by-product recovery unit. Here, SO2 is converted into a saleable product, such as sulphuric acid, elemental sulphur or gypsum (Dene and others, 2008a,b; Miyagawa and Miya, 2008; Peters, 2010, 2011).

SO2 removal efficiency has approached 99% in some low sulphur coal commercial installations, with SO2 inlet concentrations up to 1300 ppm (Dene and others, 2008a). Permit levels for the 600 MW Isogo Unit 2, which combusts low sulphur coal, are 10 ppm, 13 ppm and 5 mg/m³ for SOx, NOx and particulates, respectively. These stringent limits have been met through the use of ReACT™, low NOx burners, SCR and a second ESP installed after the ReACT™ system. Actual emissions are 2 ppm (0.0026 kg/GJ or 0.006 lb/MMBtu) SOx, 7 ppm (0.0043 kg/GJ or 0.01 lb/MMBtu) NOx, and 2 mg/m³ (0.00086 kg/GJ or 0.002 lb/MMBtu) particulates. In addition, well over 90% of the elemental and

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**Figure 8** ReACT™ process (Peters, 2011)
oxidised mercury is removed. A demonstration of ReACT™ on a slipstream from the Valmy power plant, NV, USA, when burning US subbituminous and bituminous coals, removed 97.6–99.9% of SO₂, 25.7–48.3% NOₓ (no ammonia was injected into the regenerator) and 97.1–99.6% mercury. Particulate emissions ranged from 0.003 to 0.0043 kg/GJ (0.007 to 0.01 lb/MMBtu). There was no difference in SO₂, NOₓ and Hg removal efficiency between the two coals (Dene and others, 2008b).

ReACT™ has not yet been commercially demonstrated at power plants burning high sulphur coals, although good results were achieved when a slipstream test was carried at Isogo Unit 1 with SO₂ concentrations up to 2000 ppm. The amount of activated coke fed to the adsorber would increase substantially with high SO₂ concentrations due to the need for more contact area to remove SO₂ from the flue gas. This results in the need for additional adsorber and regenerator modules, and supplementary solids conveying equipment. Also, the amount of sulphuric acid by-product increases with the amount of SO₂ removed, resulting in increased sulphuric acid production plant costs (Dene and others, 2008a).

The ReACT™ system is a dry process (no water is required for humidification or saturation of the flue gas), and so it is especially suited for sites with water use, treatment or discharge issues. It is easy to maintain, consumes ~0.7% of the plant’s gross output (Tavoulareas and Jozewicz, 2005), has a good turndown capability, and can be adapted to meet limited space requirements. The performance of the adsorption process improves with lower flue gas temperature, so reduced temperatures from turndown or seasonal variations improve the SO₂ removal efficiency. SO₂ performance compliance is immediate from boiler start-up (Peters, 2011), but NOₓ emissions may be higher due to the time it takes the absorber to reach the operating temperature required for denitrification (Tavoulareas and Jozewicz, 2005). No solid or liquid wastes are produced. The fines separated from the regenerated activated coke can be burned as a fuel or sold and used in industrial applications, such as carbon sorbents (Peters, 2010). The spent activated coke can be sold and utilised in other applications (Miyagawa and Miya, 2008). Mercury can be recovered off-site from the activated coke from the mercury zone in the regenerator and sold for commercial use; <14 t/y of activated coke from this zone would be generated in a 250 MW plant (Peters, 2010). A saleable by-product (such as sulphuric acid) is produced, and pre-collection of the fly ash means it can also be sold. Operating costs include the replacement of activated coke lost in the process through mechanical wear. The supply rate is <1.5% of the circulating rate of the activated coke. Activated coke make-up for a 250 MW plant is ~1135 t/y (Peters, 2010).

Unlike wet FGD processes, ReACT™ does not decrease the flue gas temperature. Hence there is no increase in stack water plumes. Some of the post-combustion CO₂ removal processes operate more efficiently and are more cost-effective when inlet SO₂ concentrations are maintained at very low levels. Thus ReACT™, with its low SO₂, NOₓ and particulate levels and the avoidance of water addition to the flue gas stream, may help to optimise CO₂ reagent life, if a post-combustion CO₂ control system is installed.

### 4.1.2 Technical developments

The activated carbon/coke sorbent can be produced from various carbonaceous precursor materials. Its performance is influenced by factors such as its surface area, pore size distribution, pore volume and abrasion resistance. Research has been ongoing into making cheaper and more efficient activated carbon/coke sorbents. This includes activated carbon sorbents produced from scrap tyres, which can be regenerated (Wojtowicz and Serio, 2000), palm shells (Sumathi and others, 2010a,b), coconut shells (Yan and others, 2012) and other biomass materials. Activated carbon fibres for removing SO₂, NO, mercury and CO₂ have also been investigated (Fan and others, 2010; Yoshikawa and others, 2005; Zhou and others, 2012). Activated carbon fibres have a larger surface area than activated carbon pellets.
Bench-scale studies by Li and others (2007, 2008, 2009) showed that the performance of activated coke is influenced by the type (and properties) of coal from which it is made, the activation agent, and activation temperature and time. Mixing coal with coal tar, and activating it with the flue gas, enhanced desulphurisation performance. The addition of metal catalysts (such as CoCl₂, CaCO₃ or V₂O₅) also improved desulphurisation capability. Research by other people have shown that activated carbon/coke impregnated with metals, such as calcium, cesium, cobalt, nickel, manganese or vanadium, can enhance desulphurisation and denitrification performance, and mercury removal (Chu and others, 2010; Fan and others, 2010; Liu and Liu, 2013; Ma and others, 2008; Sumathi and others 2010a,b; Tao and others, 2012). Catalytic sorbents for multi-pollutant control are reviewed by Liu and others (2010). They include the use of V₂O₅-activated carbon/coke honeycomb sorbents. These are designed to reduce fly ash plugging that can occur with granular activated carbon sorbents.

Liu and others (2010) also discuss developments in the regeneration of V₂O₅-based sorbents. Furthermore, research is being carried out in China on the regeneration of spent activated coke using a liquid instead of a thermal process (Chen and Liu, 2011). Regeneration of the V₂O₅/activated coke sorbent (after desulphurisation) by hydrogen was found to be possible with the addition of cobalt and/or molybdenum into the sorbent, and recycling the tail gas back to the reactor. Elemental sulphur is produced. Thus a separate reactor for producing elemental sulphur is avoided, lowering the overall cost of SO₂ removal (Xing and others, 2007).

4.2 SNOX™ process

SNOX™ (also called WSA-SNOX™) is a dry catalytic process, developed by Haldor Topsøe, to control SOx and NOx emissions. Large SNOX™ units in use include those on a 300 MW coal-fired power plant (Nordjyllandværket) in Denmark (since 1991), a petcoke-fired power plant in Italy, and a heavy residual fuel oil power plant in Austria. Over 100 units, including those employing just the desulphurisation step, are operating worldwide treating a range of sulphur containing offgases. SNOX™ has also been demonstrated on a slipstream (equivalent to 35 MWe) at the Niles Station, OH, USA, burning high sulphur (2.9%) bituminous coal (NETL, 2000a). The process is designed for high sulphur fuels, and is only economically attractive for plants burning these fuels. Up to 99% of SO₂ and SO₃, up to 99% of NOx and essentially all the particulates are removed (Schoubye and Ibæk, 2012), and a saleable by-product is produced.

The SNOX™ unit is located downstream of the particulate control device. The dedusted flue gas (see Figure 9) is reheated in a heat exchanger to ~400°C and ammonia is injected before the gas enters the NOx reduction reactor. Here NOx is reduced by the ammonia over a proprietary catalyst to nitrogen and water, just as in conventional SCR operation. The flue gas is then heated and SO₂ is catalytically oxidised to SO₃ in a second reactor. Designs where the two catalytic reactors are integrated into a single unit are also employed. The flue gas exiting the oxidation reactor passes through the hot side of the heat exchanger where it is cooled as the incoming flue gas is heated. SO₃ reacts with water in the flue gas to form sulphuric acid vapour, which is then condensed into 94–95% concentrated sulphuric acid in the WSA (Wet gas Sulphuric Acid) condenser. The cooling air discharged from the WSA condenser can be used in the boiler as combustion air. Boiler modifications will be necessary in SNOX™ retrofits to enable full integration of the heat recovery features, particularly for the use of preheated air (WSA cooling air) as boiler combustion air.

The flue gas needs to be cleaned to below 2 mg/m³ in order to protect the SCR catalyst. This means that particulate emissions are very low as particulates are further removed by capture on the catalyst or in condensation of the sulphuric acid. The catalyst may need to be cleaned at intervals. A catalyst lifetime of up to ten years can be expected (Haldor Topsøe, 2006; Schoubye and Jensen, 2007). Haldor Topsøe is developing new SCR catalysts and catalytic ceramic filter technology (see Section 4.3.2) to avoid catalyst deactivation and to extend the catalyst lifetime (Lindenhoff, 2011). Surplus ammonia is used in the SCR reactor to achieve a high NOx reduction efficiency without any problems with
ammonia slip, as all the ammonia in the gas after the SCR reactor is oxidised in the SO₂ oxidation reactor to nitrogen and water vapour (NETL, 2000a). The efficiency of the SO₂ to SO₃ oxidation determines the SOx removal efficiency since all SO₃ is hydrated.

No wastewater is produced since SNOX™ consumes no water, and no waste products are generated, only very low quantities of catalyst degradation fines and flue gas ash (NETL, 2000a). The only chemical consumed is ammonia. A saleable by-product is produced; each kg of SO₂ raw gas emissions leads to 2.2 kg of saleable quality sulphuric acid (Hiete and Schulte-Beeerbühl, 2012). Furthermore, boiler thermal efficiency and gross power production are increased since the heat produced by the exothermic reactions and by cooling the flue gas is recovered as steam (and heat). As a consequence, CO₂ emissions are lower. Moreover, no CO₂ is generated in the desulphurisation process, unlike limestone wet scrubbers. Typically each per cent of sulphur in the fuel increases thermal efficiency and steam production by 1% (Schoubye and Ibæk, 2012). When the coal contains 2–3% sulphur, the steam production can compensate for the power consumption of the SNOX™ process. It was estimated that for a 500 MW coal-fired power plant, the heat recovery is more than the supplemental power (12.5 MWe) needed for the SNOX™ plant, and could provide a potential net gain equivalent to 8 MWe (NETL, 2000a).

The operating cost of a SNOX™ unit decreases with increasing SOx content in the flue gas due to heat recovery, even before credits for sulphuric acid sales (Halder Topsøe, 2006; Schoubye and Jensen, 2007). Operating costs for a 300 MWe power plant firing petcoke in a downshot boiler are 600,000 US$/y (assuming ammonia costs 300 US$/t), but is outweighed by sulphuric acid sales (at 30 US$/t) of 3.6 million US$/y, giving a net operating income of 3 million US$/y (Lindenhoff, 2011). SNOX™ has lower capital requirements and lower O&M costs than a wet limestone FGD + SCR plant burning high sulphur (2.9% S) coals (NETL, 2000a). Treating low and medium sulphur coals, though, will cost more than a wet limestone scrubber (Lindenhoff, 2011). However, SNOX™ requires more space than a typical wet FGD or SCR unit (NETL, 2000a). More information about the process can be found on Haldor Topsøe’s website, www.topsoe.com/business_areas/gasification_based/Processes/SNOX.aspx.
4.3 Catalytic filter systems

Fabric filters (also called baghouses) and ceramic filters can capture over 99.9% of particulate matter, including PM$_{2.5}$. These become multi-pollutant systems when combined with sorbent injection to remove additional pollutants, such as mercury, SOx and other acid gases. NOx can be removed via SCR catalysts incorporated in the filter elements and upstream injection of ammonia or, if the temperature is sufficiently high, urea. This section concentrates on systems that include the NOx removal component. Typically, they would be installed between the economiser and air heater due to the higher flue gas temperature required for the NOx reduction reactions.

4.3.1 Catalytic fabric filters

The SNRB™ (SOx-NOx-Rox Box) process, developed in the 1970s and 1980s by Babcock & Wilcox, removes SO$_2$, NOx and particulates in one unit by combining alkali sorbent injection with a high temperature fabric filter. NOx is removed by injecting ammonia to selectively reduce NOx on the cylindrical monolith SCR catalyst (zeolite) contained within the ceramic bags (US DOE, 1999). The system operates at a temperature of ~425–455°C. The technology was demonstrated in 1992-93 on a 5 MW slipstream at the RE Burger power plant, OH, USA. Two types of bag filter were tested, a woven ceramic design and a glass fibre material. The collected particulates were removed from the bags by a high pressure air blast entering the top of the bag tube. The shock of air causes a wave of expansion to travel down the fabric, flexing the bag, which shatters and discharges the dust cake. Due to the rapid release of the air blast and the short time (<1 s) it takes to travel down the bag, pulse jet fabric filters can operate continuously. NOx removal efficiencies of over 90% were achieved with an ammonia slip of less than 5 ppm. SO$_2$ removal was 80–90% with calcium-based sorbents, and over 90% with sodium bicarbonate injection. Over 99.9% of particulates were captured. It was suggested that for power plants where high levels of NOx are produced, it may be advantageous to employ low NOx burners in conjunction with SNRB™ to reduce the catalyst requirements and minimise the fabric filter pressure drop (NETL, 2000b; Tavoulareas and Jozewicz, 2005). However, the technology does not appear to have been developed any further or tested at a larger scale.

More recently, systems have been developed that incorporate nano-sized particles throughout the walls of the fabric filter elements. These systems have been applied to small-scale plants, such as incinerators, but have not yet been demonstrated on a pulverised coal-fired power plant. An example is the Gore® DeNOx filter system, developed by W L Gore & Associates, where the catalyst is attached to the expanded polytetrafluoroethylene felt fabric filter. Aqueous ammonia is injected upstream to remove NOx by catalytic reduction. Dry alkali sorbent injection, such as sodium bicarbonate, removes SO$_2$ to limit poisoning of the catalyst, and the unwanted oxidation of SO$_2$ to SO$_3$. A Gore-Tex® membrane on the outside of the bag tube prevents the particulates from reaching the catalyst, thus avoiding dust issues such as plugging. NOx removal efficiencies of up to 90% at a flue gas temperature of 220°C, with an ammonia slip of <5 mg/m$^3$, were achieved on a municipal waste incinerator installation. Particulate emissions were less than 1 mg/m$^3$. The catalyst is regenerated by external washing, and its lifetime is >5 y (Ebert and Piccinin, 2012; Wong and Petzoldt, 2012). Some of the advantages and disadvantages discussed in the following section are applicable to this technology.

4.3.2 Catalytic ceramic filters

Ceramic filters, also called candle filters because of their solid tube shape, have been in pollution control for decades. Advanced low density ceramic filters, both with and without an embedded SCR catalyst, have been developed for multi-pollutant control. Catalytic ceramic systems include Cerafil® TopKat, developed by Haldor Tropsøe and Clear Edge Filtration (see www.clear-edge.com). Clear Edge Filtration (formerly Madison Filter) also supplies the ceramic filter elements to Tri-Mer...
Corporation, who market the system under the UltraCat™ trade name (see www.tri-mer.com) and to Maguin (see www.maguin.com) who build filtration systems under the name CerCat®. There are, as yet, no installations on large-scale pulverised coal fired power plants. The target market has been smaller applications, such coal and biomass boilers, waste incinerators, glass furnaces and other industrial plants. High density ceramic filters, though, have been employed at coal gasification and pressurised fluidised bed combustion power plants for high temperature particulate removal. This section will only discuss low density catalytic ceramic filters.

Low density ceramic filters are made from refractory ceramic fibres (typically with a fibre diameter of ~3 µm) that are formed into a rigid tube-shaped fibrous filter element (Startin and Elliott, 2009). The filter elements are installed as an alternative to conventional pulse jet cleaned fabric filter elements. Dry calcium- or sodium-based sorbents are injected into the flue gas upstream of the ceramic filter for SO₂ removal. Activated carbon or brominated activated carbon could also be injected to remove mercury. The flue gas is drawn through the filter tube wall by an ID fan where the collected particulates build up as a cake on the outside of the tube (see Figure 10). NOx is removed by catalytic reduction with injected ammonia or urea to form nitrogen and water; the catalyst is embedded within the filter walls. The clean flue gas then passes up the tube into the plenum. The cake is periodically cleaned from the filter walls online using standard pulse jet methods. The intensity of the pulse needs to be controlled so that no fibres are released from the filter structure (Heidenreich, 2013).

Ceramic filters must operate above the condensation temperature of the pollutants. Typical operating temperatures are around 180–370ºC, above which the effectiveness of the catalyst is reduced. The lower temperature is to avoid the formation of ammonium bisulphate at the catalyst. Ceramic filters without a catalyst can operate at a higher temperature, typically around 150–650ºC (Moss, 2011, 2012a).

Depending on the application, SO₂ and HCl removal efficiencies of over 90%, and as high as 97%, have been achieved with sodium-based sorbent injection (Moss 2011). Sodium-based sorbents additionally remove some of the SO₃ (>90% with trona) and mercury, whereas calcium-based sorbents only remove SO₂ and SO₃. Care, though, is required to avoid the formation of liquid sodium bisulphate, which can adhere to duct surfaces and other downstream equipment, when sodium-based sorbents are employed. The sorbent must be milled to a small particle size to maximize surface area for maximum reactivity. SO₂ reacts with the sorbent within the duct and the reaction continues in the filter cake, hence leading to higher removal efficiencies and at a lower sorbent rate than sorbent injection plus ESP systems (such as TOXECON™ – see Section 4.4.2). Over 95% of NOx is reduced by the SCR catalyst system. About 80–95% of mercury can be removed under the right conditions. Generally, activated carbon becomes less effective at temperatures above ~200ºC. Brominated activated carbons are more effective at higher temperatures of around 260–430ºC. New mercury sorbents are under development. Over 99.8% of particulates (including PM₂.₅ and below) are captured, reducing the particulate level at the ceramic filter outlet to below 2 mg/m³ (Moss, 2011).

Figure 10 Ceramic fibre filter tube with embedded nano-catalysts (Moss, 2012a)
Catalytic ceramic filters have a small footprint and are simple to operate. They could replace an existing ESP and eliminate the need for a separate SCR unit. So they could be retrofitted in power plants where there is not enough space to fit a conventional SCR unit. The filter elements have a high porosity and high thermal shock resistance, and are corrosion resistant (Moss, 2011). However, mechanical strength can be low and the risk of filter breakages is correspondingly high (Heidenreich, 2013). The modular design of the housing units allows filters to be configured to handle large gas flow volumes. The systems can be designed so that a single module can be taken off line if required, and the remaining two or more modules will continue to operate at a slightly higher pressure (designed into the fan) without interruption of the process itself and with no appreciable change in emission control performance (Moss, 2012b). This would allow some load following capability. Parasitic power consumption would probably be similar to the TOXECON™ system (see Section 4.4.2), but with the advantage of NOx removal. Costs are expected to be lower than a conventional SCR + ESP/fabric filter system.

Since the pollutants would be removed before the air heater in power plant applications, fouling and corrosion potential are substantially reduced, allowing the air heater to operate at a lower flue gas outlet temperature. A further advantage is the potential for enhanced energy recovery and improved boiler efficiency. This could lower the parasitic power consumption. Unlike conventional SCR systems, there is little oxidation of SO2 to SO3 since most of the SO2 is removed upstream of the catalyst. Consequently, poisoning of SCR catalysts, and fouling of downstream equipment due to the reaction of SO3 with ammonia are mostly avoided. Potential corrosion problems due to the formation of sulphuric acid from the reaction of SO3 with moisture in the flue gas are also prevented. In addition, the catalyst is unaffected by dust issues, such as plugging, as the particulates cannot reach the embedded catalyst. The micro-sized catalyst particles are distributed across the entire wall thickness, thus creating a large catalytic surface area. Their micro-porous structure and small size partly accounts for the increased reactivity at lower temperatures, since the diffusion restriction with the pellet or monolithic catalysts in conventional SCR units is eliminated (Moss, 2012a). Smaller amounts of catalyst are therefore required. But, like conventional SCR systems, ammonia is emitted. Furthermore, SO2 removal efficiency is lower than limestone wet scrubbers (see Section 2.1). Like other FGD processes that utilise a carbonate-based reagent (such as limestone, sodium carbonate, sodium bicarbonate and trona), CO2 emissions would increase due to CO2 formation in the chemical reactions of the reagent with SO2.

No water is consumed in the process and so no wastewater is produced. However, the fly ash cannot be sold as it is contaminated with spent and unused sorbents, and compounds such as mercury. Waste disposal could be expensive. There is also the disposal of the catalytic ceramic filters when they reach the end of their life. The catalyst lifetime is expected to be higher than in high dust conventional SCR systems. Typical life of ceramic filters is five to ten years (Moss, 2012a). A demonstration of catalytic filters on a pulverised coal-fired power plant is required to prove their applicability and performance.

### 4.4 Sorbent injection with ESP/fabric filters

Sorbent injection can be combined with a downstream ESP or fabric filter to remove the targeted gaseous pollutant(s) and particulates. This section examines two technologies that are designed to remove mercury and particulates. More information about ESPs and fabric filters can be found in the IEA Clean Coal Centre report by Nicol (2013).

#### 4.4.1 Max-9™

An electrostatically stimulated fabric filter (ESFF) has been patented by the US EPA and marketed as Max-9™ by General Electric under an exclusive licence. It combines high-voltage discharge electrodes and fabric filters in a common casing. Particulate-laden flue gas enters the unit and travels...
up through rows of filters. Each of the filters is enclosed in a grid of discharge electrodes, which ionise the particulates. The charged particulates move to the surface of the filter bag where they are retained. Since the particulates are all negatively charged, they repel each other creating a porous filter cake that allows the gas to flow more freely through the filter. A porous filter cake results in a low pressure drop, low frequency cleaning, prolonged filter life, a higher air-to-cloth ratio, and can eliminate the need to install a bigger ID fan (Nicol, 2013; Taylor, 2006).

Collection efficiencies of 99.99% of particulates have been achieved in field tests. Max-9™ can additionally capture 50–85% of the mercury without activated carbon sorbent injection. It has the potential to achieve >90% mercury removal when combined with General Electric’s staged combustion process that increases the amount of mercury absorbed by the fly ash (Modern Power Systems, 2005). Field trials showed that injecting activated carbon at an injection rate of around 48–64 mg/m³ (3 to 4 lb/macf) can remove over 90% of total mercury when the gas temperature is above 150ºC. Injecting brominated activated carbon into the flue gas removed over 90% of total mercury at about half the injection rate for the activated carbon, when firing low chlorine bituminous coal (Taylor, 2006).

The mercury-containing fly ash cannot be sold for use in concrete, and would need to be landfilled, at a cost. The fly ash can be treated to remove the mercury to lower disposal costs. This is discussed in the following section. Non-carbon based sorbents and ‘concrete compatible’ carbon sorbents are being developed that do not adversely affect fly ash marketability. When installed after a particulate control device, Max-9™ can be used as a polishing filter for fine particulates and mercury removal. This would enable most of the fly ash (~99%) to be sold. More information about the system can be found at www.ge.com/mining/sol_environmentaltech.html.

### 4.4.2 TOXECON™ technology

EPRI has developed two technologies, TOXECON™ and TOXECON II™, for removing mercury and fine particulates. TOXECON™ (toxic emission control process) consists of a sorbent injection system and a compact pulse jet fabric filter, with the sorbent being injected into the duct before the fabric filter. The technology is intended for installation downstream of an existing ESP. In a hot-side ESP configuration, the TOXECON™ system is placed after the air heater. In the case of a cold-side ESP installation, the TOXECON™ system is located downstream of the ESP (see Figure 11a). The filter cake on the fabric filter provides additional time and contact between the sorbent and flue gas, and so less activated carbon may be needed and/or a higher mercury removal efficiency may be achieved than through injection upstream of the ESP. In TOXECON II™ (see Figure 11b), the sorbent is injected into the back portion of a cold-side ESP. It offers some of the benefits of TOXECON™ but at a lower capital cost. TOXECON™ has been installed at eight plants (NETL, 2012). Licensed suppliers of the TOXECON™ technologies include Babcock & Wilcox, and Hamon Research-Cottrell.

The first full-scale commercial TOXECON™ demonstration was at the subbituminous coal (PRB) fired Presque Isle power plant in Marquette, MI, USA. The flue gas from three 90 MW units was combined and treated in a single TOXECON™ fabric filter. The hot-side ESP captured over 99% of the particulates, with over 85% of the remaining fine particulates and spent sorbent removed in the fabric filter (NETL, 2010). Injecting activated carbon or brominated activated carbon removed over 90% of the mercury at an injection rate of less than 48 mg/m³ (3 lb/macf). Less brominated activated carbon was required to achieved the same capture efficiency as the activated carbon. Parametric testing showed that removal rates for both sorbents deteriorated as flue gas temperatures increased. Simultaneous injection of trona (a sodium bicarbonate mineral) at an injection rate of 2688 kg/h (5926 lb/h) reduced SO₂ emissions by 70%, but unfortunately decreased mercury removal and gave little reduction in NOx emissions. It was estimated that around three times the amount of activated carbon would be needed to maintain a 90% mercury capture rate with trona injection. The cleaning frequency of the fabric filter increased with the increased particulate loading from sorbent injection,
shortening the bag life. Also, spontaneous combustion of the collected fly ash and activated carbon occurred in the fabric filter hoppers. Continuously removing the solids from the hoppers will mitigate the fire risk. Total capital requirements for retrofitting TOXECON™ are estimated to be US$41.7 million or 154 $/kW (US$2009). O&M costs would be $1.4 million, about 75% of which is due to the cost of activated carbon and increased ID fan power. The levelised cost for 90% mercury removal is 168,024 $/kg (76,214 $/lb) of mercury removed with a capital cost of 139,309 $/kg (63,189 $/lb) of mercury removed. Mercury removal at the Presque Isle power plant averages ~44 kg (97 lb) per year (Derenne and Stewart, 2009). Capital costs will be site specific for retrofit TOXECON™ installations. Costs will be lower in new plant applications.

Capital costs for a TOXECON II™ system are lower than a TOXECON™ system as only minor retrofits to the existing ESP for the sorbent injection system are required instead of installing a separate fabric filter. However, fine particulate capture will not increase. A demonstration of TOXECON II™ at the subbituminous coal (PRB) fired Independence power plant in Newark, AR, USA, captured 90% of the mercury at an injection rate of 88 mg/m³ (5.5 lb/macf) with brominated activated carbon (Campbell and others, 2007). However, the injection grid was prone to plugging. On-site milling of the sorbent reduced the injection rate (Sjostrom and others, 2008). Parametric tests indicated that 90% mercury capture was possible at the Limestone power plant in Jewett, TX, USA, when burning a lignite/subbituminous coal blend. This was not achieved in practice. This was partly due to the poor sorbent distribution in the ESP. Ensuring proper sorbent distribution is critical for effective mercury control. Varying the boiler load can significantly impact the sorbent distribution, and consequently load following may be an issue. Improved injection lance design may increase mercury capture (Dombrowski and others, 2007).

Mercury removal efficiency using activated carbon sorbents is dependent on a number of factors, including flue gas temperature, residence time, sorbent distribution and flue gas SO₃ concentration. Higher levels of SO₃ from burning high sulphur coals or SO₃ injection to improve fly ash resistivity...
(for improving capture in ESPs) can adversely affect mercury capture in TOXECON II™ installations. This is due to the competition for capture sites on the activated carbon. Injecting an activated carbon sorbent that also contains an alkaline material to capture and neutralise SO₃ could improve mercury capture (Feeley and others, 2009). But injection of trona meant that the injection rate of activated carbon at the Presque Isle power plant had to be increased to maintain a 90% mercury removal rate.

A significant advantage with the TOXECON™ technologies is that the majority of the fly ash can still be sold for concrete or other applications. Around 99% of the fly ash is captured in the existing ESP in the TOXECON™ system (URS Corp, 2008) and ~90% of the fly ash is removed in the front portion of the ESP with TOXECON II™ (Campbell and others, 2007). Therefore only a small portion of the captured fly ash will be unsaleable because it is rich in mercury, carbon and other contaminants. For a 500 MW plant using TOXECON™, this stream would probably amount to around 45–90 kg/h (100–200 lb/h) or about 726 t/year (800 tons/y). If TOXECON II™ was installed, then about 230–455 kg (500–1000 lb/h) or ~3628 t/year (4000 ton/y) would be produced. The material will be similar to that from TOXECON™, but with a higher fly ash content and lower mercury concentration (URS Corp, 2008). It would have to be landfilled, unless the mercury is removed using a thermal desorption method. The resultant carbon material can be recycled back into the system by blending with fresh activated carbon (NETL, 2010; Okwadha and others, 2009). Otherwise the carbon material could be sold. A process was designed that uses it to manufacture nitrogen-based fertiliser (NETL, 2010). Non-carbon based sorbents and ‘concrete compatible’ carbon sorbents are under development that may enable all of the fly ash to be sold.

No significant impacts on FGD by-products from a downstream FGD system would be expected with a TOXECON™ system because of the relatively low activated carbon injection rate required upstream of the fabric filter compared to an ESP, and because the fabric filter should capture activated carbon at a high efficiency (URS Corp, 2008). However in the TOXECON II™ system, injecting sorbents into the ESP may result in increased particulate emissions at the ESP outlet, and the fine particulates are not removed. The particulates are captured in units which have a downstream scrubber. Consequently stack particulate emissions would not increase, but the gypsum by-product (from a limestone wet scrubber) may became unsaleable (Dombrowski and others, 2007).

4.5 Comments

Since all the technologies discussed are dry, no wastewater is produced and therefore no expensive wastewater treatment plants are needed. The processes (except SNRBTM) are commercially available, although the Gore® system and catalytic ceramic filters have not yet been demonstrated on a large-scale coal-fired power plant. The technologies are designed to remove different pollutants. Both ReACT™ and SNOX™ remove sulphur oxides and nitrogen oxides, and act as a polishing device for particulate matter. Although ReACT™ has a lower NOx removal efficiency than SNOX™, it does capture mercury. SNOX™ is only economically attractive for plants burning high sulphur coals – it was designed for high sulphur fuels. On the other hand, ReACT™ is more suitable for low to medium sulphur coals.

Max-9™ and the TOXECON™ technologies combine sorbent injection with a particulate control device to remove mercury and particulates. Injection of trona additionally removes SOx but increases the sorbent injection rate required to achieve 90% mercury capture. Sorbents can be injected before the catalytic ceramic filter. These contain an embedded catalyst designed to remove NOx with ammonia injection.

ReACT™ and SNOX™ are the only technologies that produce saleable by-products. Since they are installed downstream of a particulate collection device, fly ash quality is unaffected, allowing the majority of the fly ash to be sold. Loss of ash sales would mean a loss in revenue and additional disposal costs for the power plant owner. However, the fly ash is contaminated with the spent and
unused sorbent in systems incorporating sorbent injection. Upstream collection of the fly ash before the sorbent injection point preserves the fly ash quality. However, TOXECON-II™ only pre-collects ~90% of the fly ash, whilst TOXECON™ collects ~99% in the upstream ESP. Thus higher disposal costs will be incurred with TOXECON-II™ systems. The application of ‘concrete compatible’ sorbents may solve this drawback. Nevertheless, injecting sorbents in TOXECON-II™ may increase particulate emissions at the ESP outlet. A downstream device for collecting the particulates may be needed in order to meet environmental regulations.
5 Non-thermal plasma technologies

Non-thermal plasmas have been applied in air pollution control systems to remove principally NOx and SO₂. Elemental mercury is also oxidised to mercury oxide (HgO), which is easier to control than elemental mercury. Non-thermal plasma is a low energy discharge state of gaseous molecules. Its energy intensity is low enough so that the temperature of the molecules and their excited species do not increase. The excited radicals and ions undergo chemical reactions with an added chemical compound (often ammonia) to convert the pollutants to useful or harmless compounds. This chapter discusses cold non-thermal plasma technologies where the flue gas is treated within the plasma reactor. The plasma is generated by electron beams, corona discharges or dielectric barrier discharges. Commercial systems where ozone is generated in a non-thermal plasma reactor and then used to oxidise NOx and mercury are covered in Chapter 6.

Hybrid systems which combine non-thermal plasma technology with integrated scrubbers have been developed. The WOWClean® process removes SOx, NOx, particulates, mercury and other heavy metals by first treating the flue gas in a reactor that incorporates a non-thermal plasma generation system and integrated scrubbing section. The flue gas then passes through two scrubber/wet ESP reactors. The process had been pilot-tested on a slip stream from a petcoke power plant and a wood-fired plant (WOW Energy, 2006), but further development seems to have ceased.

5.1 Electron beam processes

The electron beam process simultaneously removes SOx and NOx through the irradiation of ammonia-rich flue gas with high energy electrons. A saleable ammonium sulphate/nitrate fertiliser by-product is produced. Up to 99% of SO₂ and ~90% of NOx can be removed when burning high sulphur lignite (Basfar and others, 2010), along with other acid gases, such as HCl and HF, polycyclic aromatic hydrocarbons (PAHs) and particulates. Additionally, up to 98% of the elemental mercury is oxidised (Kim and others, 2008).

The electron beam-flue gas treatment (EB-FGT) technology, also termed E-Beam, is at an early commercial stage. It has been pilot-tested at coal-fired plants in Japan, the USA, China, Germany, Poland and Bulgaria, and various industrial plants. There are (or were) commercial applications on the Chengdu, Hangzhou and Jingfeng power plants in China and the Pomorzany power plant in Szczecin, Poland, all coal-fired. The EB-FGT systems at the Chengdu and Hangzhou plants (now closed) were developed by the Ebara Corporation, Japan, and the Jingfeng plant by Sichuan Entech Environment Technology Co Ltd, which is controlled by the Institute of Environmental Protection Engineering (Mao, 2005). The Pomorzany power plant uses a similar process developed by the Polish Institute of Nuclear Chemistry and Technology. The main technical parameters of the plants are given in Table 4. The Chinese plants were designed primarily for desulphurisation; hence the low NOx removal efficiency. A further application at the 165 MW Sviloza lignite-fired cogeneration power plant in Bulgaria is planned (Kim and others, 2009, 2011), but is on hold because of the financial crisis. PAVAC Industries has signed an agreement with SaskPower and with Sustainable Development Technology Canada, a federal funding agency, to install and operate its EB-FGT system at an existing Canadian power plant (Edinger, 2012).

In the EB-FGT process (see Figure 12), the flue gas from the particulate collector is cooled and humidified, typically in a spray cooler where water is injected into the flue gas. Ammonia is added as an aqueous solution to the spray cooler and/or as a gas before the irradiation reactor. The low temperature (65–80°C), wet (10–15% humidity) and ammonia-rich flue gas then enters the irradiation reactor, where high energy electrons react with molecules in the flue gas to produce radicals that then react with the SOx and NOx to produce sulphuric and nitric acids, respectively. These acids, in turn,
react with the ammonia to form ammonium sulphate and ammonium nitrate. The ammonium sulphate/nitrate and other particulates are collected in a downstream ESP or fabric filter, and sold as fertiliser. The chemical reactions are completed within seconds. The cleaned flue gas is reheated before being emitted through a wet stack to avoid condensation problems and improve stack gas dispersion.

The EB-FGT processes differ mainly 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. The EB-FGT processes listed in Table 4 capture the ammonium sulphate/nitrate particles in a dry ESP. Instead, the e-SCRUB™ Process, developed by eScrub Systems Inc, uses a wet ESP to collect the ammonium sulphate/nitrate into a brine solution. The brine solution is recycled to the spray dryer, where the flue gas is cooled, before entering the electron beam reactor. Work on the process appears to have ceased and therefore it will not be discussed any further.

High removal efficiencies of 90–99% for SO₂ and 70–90% for NOx have been achieved. The removal efficiency mainly depends on inlet emission concentration, ammonia injection stoichiometry, irradiation dose and flue gas temperature. Capturing 90% of SO₂ requires a minimum of

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<tbody>
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<td>90</td>
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<tr>
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<td>20</td>
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<td>8–12</td>
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<td>160 (7.35)</td>
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<tr>
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<td>1.7</td>
<td>4.9</td>
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</tr>
</tbody>
</table>

* 1 kGy = 1 kJ/kg; † dollar year is not given

Table 4 Main technical parameters of EB-FGT on coal-fired power plants (Mao, 2005; PlasTEP, 2011)
2 kGy (1 kGy = 1 kJ/kg flue gas). NOx removal needs a higher radiation dosage, with a dose of ~2–7 kGy required to remove 50%. Capturing 80% of NOx needs at least 10 kGy (UNEP, 2010). SO2 removal efficiency increases with decreasing flue gas temperature, the reverse for NOx removal (Chmielewski and others, 2004; UNEP, 2010). A higher SO2 concentration also improves NOx removal, making the process better suited for high sulphur coals.

The process additionally captures around 27% (on average) of the sixteen PAHs classified as priority pollutants by the US EPA. The removal efficiencies for fourteen of the individual PAH compounds ranged from 2% (benzofluoranthene) to 96.5% (for acenaphthene). The concentrations of anthracene and fluoranthene, though, increased probably because of decomposition of higher-ring PAHs (Basfar and others, 2010). A review on volatile organic compounds removal from gaseous wastes using electron beam technology by Sun and Chmielewski (2012) reports that the removal efficiencies of PAHs ranged from 40% up to 98% at a pilot plant in Poland. PAH removal from a pilot plant in Bulgaria burning lignite achieved 85% (wt/wt) at a radiation dose of 4 kGy.

CO2 is not generated in the removal process, unlike limestone wet scrubbers (see Section 2.1) where CO2 is a by-product of the reaction of calcium carbonate with SO2. The high SOx removal rate means that power plants with an installed EB-FGT system may help optimise CO2 reagent life if a post-combustion CO2 control system is installed. But treating flue gas with ammonia leads to ammonia emissions. Ammonia slip is estimated to be 40 ppm at the planned 120 MWe Sviloza power plant in Bulgaria with a flue gas flow rate of 600,000 m3/h (Kim and others, 2011).

The ammonium sulphate/nitrate by-product is dry, and only requires granulation to produce saleable fertiliser. Fertiliser contaminants include ammonium chloride (from chlorine forming compounds in the coal), heavy metals (including mercury) and PAHs. The contaminant levels (especially the heavy metals), though, are lower than in conventional commercial fertilisers (Chmielewski and others, 2004). Moreover, no solid wastes that require landfilling are produced. Nevertheless, the ammonium sulphate/nitrate particles are small and sticky, and therefore appropriate action is required to avoid problems in their collection in ESPs or fabric filters. Since the EB-FGT system is installed downstream of the particulate control device, the quality of the fly ash is unaffected and could still be sold.

Although the actual electron beam scrubbing process is dry, the overall water consumption is relatively high. This is because water is consumed in the spray cooling tower to quench and humidify the flue gas, and to cool the electron beam reaction unit (when necessary). A 65 MW boiler with a flue gas flow of 300,000 m3/h and removing 98% SO2 and 70% NOx consumes 108 t/d of water and 48 MWh/d of electric power (PlasTEP, 2011). Washing the deposits off the reactor bottom generates a small amount of wastewater. At the Maritza East 2 pilot plant in Bulgaria, the wastewater along with condensate from the outlet protection, was sent to the plant’s water treatment system (Kim and others, 2011).
A life cycle inventory analysis was carried out by PasTEP (2011) to assess the environmental impact of EB-FGT compared to a limestone wet FGD + SCR system. It was found that, within the chosen system boundaries, EB-FGT performed better with respect to the acidification (acid deposition) and human toxicity potentials. Wet FGD + SCR was more favourable in terms of the global warming potential, ozone layer depletion (thinning of the stratospheric ozone layer) and eutrophication potential (where nutrient enrichment may cause an undesirable shift in species composition and elevated biomass production in both aquatic and terrestrial ecosystems). Most of the impacts were associated with the utilisation of ammonia in the EB-FGT reactor and SCR unit. The environmental impact of using the ammonium sulphate/nitrate by-products as fertilisers contributed to EB-FGT’s more favourable scores, whilst its higher global warming potential resulted from its higher electricity and ammonia consumption. It was assumed that all the gypsum formed in the wet FGD process was landfilled.

The EB-FGT system has good load-following capability (PlasTEP, 2011), and the small footprint enables the system to be more easily retrofitted than a conventional wet FGD + SCR system. However, the availability of the process cannot meet the requirement of power plant operators who normally require a pollutant control system to be available for 95% or more of a power plant’s operating hours (Zhu, 2010). The EB-FGT systems on the Chengdu and Hangzhou power plants were closed down because of serious erosion, high energy consumption, ammonia pollution and low running reliability (Gao and others, 2008). EB-FGT has lower capital and operating costs than a wet FGD + SCR system (but higher than just a wet FGD system). The investment cost for a retrofit 120 MWe unit is 160 US$/kWe and the annual operating cost is 7.35 US$/kWe for EB-FGT (based on data from the Pomorzany plant). This compares to investment and operating costs of 230 US$/kWe and 7.6 US$/kWe for wet FGD + SCR (Tyminski and Pawelec, 2005). A 2006 paper quoted by Kim and others (2009) estimated the unit capital and operating costs for the planned 165 MW Sviloza plant at 227 US$/kWe and 21.2 US$/kWe (157 US$/tSO₂), respectively. Table 4 gives the capital and operating costs for four EB-FGT demonstration plants (the dollar year is not given). The operating costs are highly reliant on the market price for the fertiliser by-product and ammonia.

Energy consumption is another important factor affecting the plant’s operating costs. The energy requirement for EB-FGT depends greatly on the NOx reduction required. When significant NOx reduction is not required, the auxiliary power for the EB-FGT process can range from 2% to 3% of the total plant output, as shown in Table 4. For example, around 2% of the Jinfeng power plant’s energy was consumed when removing 90% SO₂ and 20% NOx. This is higher than a wet FGD system where parasitic power consumption is 1.5% or less (Mao, 2005). When NOx reduction is above 60%, the auxiliary power may reach 5% of total power plant output (UNEP, 2010). Generally, the higher the sulphur content in the flue gas, the more economic the process becomes.

The limited acceptance of the EB-FGT technology is seen by the lack of new installations on power plants since the 2005 Jingfeng demonstration unit. This may be due to the relatively high investment and maintenance costs, and high auxiliary power consumption. The electron beam accelerator forms a large component of the capital cost (along with the ESP). The four accelerators for the planned Sviloza plant will cost about US$8 million out of the total US$37.4 million (€26 million) capital cost (Kim and others, 2009). Large-scale deployment of the technology will require further development of the accelerators with the emphasis on higher beam power, higher electrical efficiency and lower capital costs (Office of High Energy Physics, 2012). Greater reliability and availability would also help. The overall aim is to achieve reliability, performance and lower costs than a conventional SOx and NOx flue gas treatment system. Currently research is being carried out into removing additional pollutants in the process.

5.2 Corona discharge technology

Corona discharge technology for controlling air pollutants, such as NOx, SO₂, HCl and mercury, has
been investigated since the 1980s. It has been demonstrated at bench- and pilot-scale for treating flue gas from coal-fired power plants, but has not yet been demonstrated at a full-scale plant. Nevertheless, the technology is applied in other industries for treating exhaust gases and water. Direct current driven corona discharges are used in ESPs for physical removal of particulates from power plant flue gas.

The technology works in a similar way to the electron beam process, described in the previous section. The main difference between the two is that the corona discharge system generates the energetic electrons within the flue gas, whereas electron beam technology generates higher energy electrons externally and then injects them into the flue gas. Corona discharge systems operate under atmospheric pressure, whilst the EB-FGT system operates under a vacuum. The energetic electrons are discharged when an electric field (direct current (DC), alternating current (AC) or pulsed) is applied to a flue gas. Studies have shown that a pulsed corona exhibits a higher removal efficiency than a DC corona for simultaneous removal of SOx and NOx, and so the emphasis in this section is on pulsed corona discharge (PCD) systems.

In the ELFI system, developed by the Vinca Institute of Nuclear Sciences in Serbia, the flue gas from the particulate collector is cooled in a spray cooler, ammonia is added, and the gas is passed into the plasma chemical reactor. Here, the generated electrons transfer energy to the gas molecules through collisions, resulting in excitation, attachment, dissociation, or ionisation that produce radicals and ions. The radicals oxidise SO2 and NO in the flue gas to, respectively, SO3 and NO2, which are then converted to sulphuric and nitric acids in the presence of water vapour. These acids, in turn, react with the ammonia to form ammonium sulphate and ammonium nitrate particles, which are recovered in a fabric filter and can be sold as an agricultural fertiliser. The ELFI technology has been demonstrated at bench-scale, and a pilot plant is planned (Miljevic and Lucic, 2007).

Pilot-scale tests of a similar system in China treated the slipstream (flow rate 12,000–20,000 m³/h) from a 3 MW coal-fired power generating boiler in a PCD reactor (Wu and others, 2003). Again, ammonia was injected into the flue gas and the ammonium sulphate/nitrate by-products were collected, in this case, in a downstream ESP. A SO2 removal efficiency of over 80% was achieved with an initial SO2 concentration of 1500–2000 ppm, and over 50% of NOx was removed (initial NO concentration was 200–800 ppm). The flue gas temperature was 70–75°C, residence time was 6–8 s and the pulse power was 3–4 Wh/m³. Ammonia slip was less than 50 ppm (SO2:NH3 stoichiometric ratio was 1:0.9 to 1:1). The investment cost of a PCD flue gas desulphurisation system was estimated to be ~10% of the investment cost of the power plant, with operating costs of ~60 US$/tSO2 removed.

A pilot plant in Korea treating 1800 m³/h of flue gas in a PCD system removed about 95% of SO2 when ammonia was added at a molar ratio of NH3 to SO2 of 2:1; ammonia slip was 26 ppm. About 70% of NOx was removed with the addition of ethylene (C₂H₄). This also lowered the energy consumption to ~9 Wh/m³. Better reaction rates are obtained with propene (C₃H₆) addition, but it is more expensive than ethylene. Encouraged by the results, Doosan built a 10 MW demonstration unit processing 35,000 m³/h of flue gas from a coal-fired power plant (Kim and others, 2003).

A different approach was taken by Yan and others (2006) where a wet reactor system (instead of a dry reactor) is used. The wet reactor is partitioned into a thermal chemical section and a plasma section. The thermal section works in a similar way to an ammonia scrubber. The flue gas from the particulate collector first passes through the thermal section where ammonia water is sprayed to absorb over 80% of the SO2. A portion of the spent solution is then recycled back to the thermal section, whilst the rest, with the flue gas, passes into the plasma section. Here a DC voltage superimposed with an AC voltage is applied to generate streamer plasmas. Further desulphurisation occurs and sulphites in the spent solution are oxidised to sulphates. The end solution is then neutralised and dried to produce a fertiliser. The cleaned gas is emitted through the stack after heat exchange with the incoming flue gas. Pilot-scale tests with a flue gas capacity of 12,000 m³/h removed over 95% SO2 (with an inlet SO2 concentration of ~500 ppm). NOx emissions were also reduced, but the emphasis was on desulphurisation. Energy consumption in the reactor was 1.8 Wh/m³. Ammonia slip was less than
5 ppm, lower than from dry plasma reactors. Additionally, the production of by-products that stick to the walls of the reactor is avoided, a problem that can occur in dry plasma reactors.

Electrical consumption of corona discharge technology can be as high as 3% of a power plant’s production capacity. A corona discharge technique whereby ammonia is fed into the reaction chamber through hollow electrodes (termed plasma corona radical shower) has a lower electrical consumption than a wire-cylinder discharge geometry. It also results in higher ammonia concentrations (and its decomposition into radicals) within the plasma corona. SO₂ removal rates of ~96% have been achieved in bench-scale experiments (Gao and others, 2008). Injecting ammonia and propene through the electrode nozzle instead of from the plasma reactor inlet increased NO and NOₓ removal rates by around 8% and 10%, respectively (Shang and Xue, 2012). Removal rates of over 60% for NO and ~50% for NOₓ were achieved with a specific input energy of 1.5 Wh/m³. A proprietary plasma corona radical shower process to remove SO₂, NOₓ and mercury from coal-fired flue gas has been developed by AirScience, SaskPower and CANMET in Canada and tested at pilot-scale.

The removal efficiencies of NOₓ, SO₂ and mercury from flue gas are mainly dependent on the input power, inlet emission concentration, ammonia injection stoichiometry, flue gas temperature and water vapour content (Gao and others, 2008; Kim and others, 2003; Wu and others, 2003; Xu and others, 2009). NOₓ removal rates increase as the input power rises. Although the corona power has some promotion for SO₂, the concentration of ammonia is more significant as SO₂ removal mainly depends on its thermo-chemical reactions with ammonia. NO, SO₂ and mercury oxidation efficiencies (and hence removal efficiency) decrease as the initial concentrations increase. Their oxidation efficiencies are enhanced at higher peak voltages since more radicals and active species are generated. Consequently, a voltage just below the sparking discharge voltage is preferred. The addition of water vapour improves SO₂ conversion efficiency but restrains both NO and mercury conversion efficiencies. The presence of NO hinders mercury oxidation due to the preferential reactions of NO with oxygen radicals and ozone (Ko and others, 2008).

PCD with ammonia and/or ethylene or propene injection can remove around 95% of SO₂ and 40–76% of NO/NOₓ from flue gas (Gao and others, 2008; Kim and others, 2003; Shang and Xue, 2012), as well as some of the mercury. An oxidation efficiency of over 55% for mercury has been achieved (Xu and others, 2009). A saleable fertiliser by-product is produced with ammonia injection, and saleable fly ash as well. The quality of the fly ash is unaffected by the PCD system since it is installed.
downstream of the particulate collection device. No waste materials that require landfilling are generated in a dry plasma reactor system. The small footprint would enable the technology to be more easily retrofitted than a wet FGD + SCR system. Operating costs are lower than a wet FGD + SCR system, but higher than the EB-FGT process (see Figure 13). But its capital costs are lower than an EB-FGT system (Zhu, 2010). However, a full-scale demonstration of a PCD system at a coal-fired power plant is required; only small-scale demonstrations have been carried out. Auxiliary power consumption is high. How to get higher pollutant removal rates at a lower energy consumption is one of the crucial issues with the technology. Injecting additives, such as propene, may increase NOx removal efficiency. There are also concerns over ammonia slip, and the adhesion of the sticky by-products on the plasma reactor wall. Appropriate action is necessary to avoid problems in the ESP or fabric filter when collecting these sticky particles.

5.3 Dielectric barrier discharge technology

Dielectric barrier discharge (DBD) technology, also known as silent discharge or partial discharge, is widely used industrially for ozone generation. The injection of ozone into flue gas for pollutant control is discussed in Chapter 6. The commercial ECO® system, which passes the flue gas through an DBD reactor, is discussed later in this section.

The technology works in a similar way to PCD, but whereas in the PCD method the transient behaviour of the plasma is controlled by the applied voltage pulse, the plasma that takes place in a DBD self-extinguishes when charge build-up on the dielectric layer reduces the local electric field. This means that a simpler electrical power supply can be used. In a DBD reactor, an AC high voltage is applied between two electrodes, one or both of which are covered with a thin dielectric layer, such as glass, quartz or ceramics. The dielectric layer limits the amount of charge and energy imparted to an individual microdischarge and, at the same time, distributes the microdischarges over the entire electrode area. It also ensures no spark or arc occurs in the discharge gap.

In a DBD reactor, NO is oxidised to NO2, a small portion of the SO2 to SO3, and elemental mercury to mercury oxide (HgO). The NO2 and SO3 then react with water vapour in the flue gas to form nitric acid and sulphuric acid, respectively. Ammonia injected into the flue gas upstream of the DBD reactor reacts with the acids to form ammonium sulphates and nitrates, which can be collected and sold as fertilisers. Otherwise, the acids and soluble SO2, NO2 and HgO can be removed in a downstream wet scrubber (as in the ECO® process – see Section 5.3.1).

Treatment of a 200 m3/h slipstream from a 200 MW coal-fired power plant in Serbia removed over 98% of SO2 when ammonia was injected into the flue gas (Obradović and others, 2011). The addition of ammonia also increased NO removal efficiency, with a higher efficiency achieved when ammonia was injected upstream of the DBD reactor (instead of downstream of the DBD and before a secondary ESP). Over 60% NOx removal was achieved by the DBD alone when treating flue gas from a diesel generator (Chang and others, 2004). This increased to 93% when the flue gas was additionally scrubbed with a sodium sulphide (Na2S) solution; the overall SO2 removal efficiency was 91%. Energy efficiencies were 17 and 18 g/kWh for NOx and SO2 removal, respectively, and 35 g/kWh for simultaneous NOx and SO2 removal. Wang and others (2010) report over 90% oxidation of elemental mercury in the DBD reactor, under their experimental conditions. About 45% mercury oxidation can be achieved with an energy input of 86 J/L, whilst nearly 100% mercury oxidation needs an energy density of 114 J/L (Mathur, 2003).

The removal efficiencies of SO2, NOx and mercury are dependent on factors such as the input energy, inlet emission concentration, ammonia injection stoichiometry (if used), flue gas temperature, water vapour content, and oxygen concentration (Chang and others, 2004; Mathur, 2003; Obradović and others, 2011; Wang and others, 2010), as discussed for the PCD system (see Section 5.2).
The main advantage of DBD reactors is their simplicity. Compared to PCD they require no sophisticated pulsing circuits and, compared to electron beam treatment, they require no vacuum chambers with delicate windows separating the acceleration chamber from the polluted flue gas-pressure environment. They can also be scaled up without additional difficulties, unlike most other discharge technologies (Kogelschatz, 2003). However, the narrow inter-electrode gap is sensitive to pluggage. Residual fly ash in the flue gas becomes charged within the EDB and could adhere to the electrodes, obstructing the gas flow. Water condensate within the DBD, though, would remove the attached ash, in a similar way to the process in wet plasma reactors (Obradović and others, 2011). Moreover, CO is generated from the decomposition of CO₂. Its emission could possibly become an issue in some cases; it more than doubled in the slipstream tests carried out by Obradović and others (2011).

5.3.1 ECO® technology

Powerspan’s Electro-Catalytic Oxidation (ECO®) technology is an integrated process that removes NOx, SO₂, SO₃, HCl and other acid gases, mercury and other heavy metals, and fine particulate matter (<PM₂.₅) in a single system. This is achieved in three steps by using a DBD reactor, an ammonia-based scrubber and a wet ESP. Saleable by-products are produced. In applications where NOx removal is not required, such as when a NOx control system is already fitted, then the ECO® technology can be installed without the DBD reactor, a process called ECO-SO₂. If CO₂ removal is needed than the ECO₂® technology can be integrated with the ECO® or ECO-SO₂ technologies. ECO₂® is a regenerative thermal swing absorption process that also uses an aqueous ammonia solution for pollutant capture.

The first demonstration of the ECO® process was built at First Energy’s R E Burger coal-fired power plant at Shadyside, OH, USA. The ECO® unit treated a 50 MWe (equivalent) slipstream from a 156 MW front wall boiler from February 2004 to December 2010. The ECO₂® technology was tested on a 1.3 MWe slipstream from the 50 MWe ECO® unit from December 2008 through 2010. Over 90% NOx, >98% SO₂, 85% oxidised mercury and 10 mg/m³ particulate matter were achieved over six months of testing of the ECO® system (EPRI, 2007). Over 90% of CO₂ was captured in the ECO₂® trials from an inlet gas containing 11–12% CO₂ (Jones, 2010; Mills, 2012). None of the ECO® technologies have yet been demonstrated at full-scale on a coal-fired power plant.

After the majority of the particulates have been removed in an ESP or fabric filter, the ECO® process (see Figure 14) passes the flue gas through a DBD reactor, where the pollutants are oxidised by the generated atomic oxygen and hydroxyl radicals to form soluble compounds that are more easily removed downstream. Nitric oxide (NO) is oxidised to NO₂ and nitric acid, a small portion of SO₂ is converted to SO₃ and sulphuric acid, and some of the mercury is oxidised to mercuric oxide (HgO). The flue gas then enters the bottom of a dual-loop wet scrubber. The lower loop cools and saturates the flue gas, and concentrates the by-products. The recycle pump circulates the ammonium sulphate reaction product to the spray nozzles, with a bleed stream to the by-products processing system. The flue gas passes through a separation tray into the upper loop where aqueous ammonia is added to scrub SO₂ and NO₂, and neutralise the acids. Ammonium sulphate, ammonium nitrate and nitrogen are formed. The liquid falls to the separation tray, where some of it flows down into the reaction tank at the bottom of the lower loop. The remainder is recycled back to the upper loop spray nozzles.

The flue gas then enters the integral wet ESP where aerosols created in the discharge reactor and ammonia scrubbing process steps, along with mercury, other air toxics and fine particulate matter, are captured and returned to the lower loop. The clean flue gas is emitted to the atmosphere through the wet stack or sent on to an ECO₂® unit. Make-up water is periodically used to rinse the walls of the wet ESP and replenish the water lost to evaporation.

The bleed stream of concentrated, clear liquid from the lower loop is passed through a filter to remove...
the ash and insoluble metals, and then through an activated carbon adsorption bed to remove the mercury for separate disposal. The resultant solution can be sold or the ammonium sulphate and ammonium nitrate are crystallised out for sale to the fertiliser industry.

The ECO-SO₂ process omits the DBD reactor, and the ammonia reagent is added to both the lower and upper loops in the wet scrubber. In the ECO₂® unit, the flue gas, at a temperature of ~60°C, moves upwards through the absorber tower where it mixes with a proprietary ammonia-based solution (which contains ammonium carbonate) flowing down over the packing. The decarbonised flue gas leaves the top of the scrubber and is emitted to the atmosphere through the wet stack. Once the CO₂ has been captured, the ammonium bicarbonate solution that is formed passes through a heat exchanger before entering the top of the regenerator, where it is heated with steam. The regenerated ammonia is then returned via the heat exchanger and a cooler to the scrubbing process. The liberated CO₂ is dried, compressed and sent for storage or utilisation. The residual water vapour removed in the dryer is returned to the CO₂ absorber (McLarnon and Jones, 2008).

Removing ammonia vapour, which is released in the scrubbing and regeneration steps, is essential to prevent it from exiting the ECO₂® plant with the flue gas (ammonia slip). Scrubbing ammonia vapour in the top of the CO₂ absorber (see Figure 14) creates a stream of aqueous ammonia that is sent to the upper loop of the ECO® scrubber (when interconnected to an ECO® unit). Ammonia in the flue gas is reduced to below 5 ppmv (McLarnon and Jones, 2008). A new, proprietary solvent that does not contain ammonia, and hence produces no ammonia vapour, has been tested (Jones, 2010).

The ECO® technology removes significant amounts of the criteria pollutants SO₂, NOx, mercury, PM₂.₅ and acid gases, in most cases, to below the regulated limits. NOx removal efficiency could be improved by injecting hydrogen peroxide upstream of the DBD reactor. Economic analysis showed that, in some commercial systems, the cost of the hydrogen peroxide reagent is more than offset by the savings achieved with the reduction in reactor power attained through the use of the reagent (Jones, 2010). Optimum performance of the ECO® process occurs when the SO₂ to NOx molar ratio is 3 or more, due to chemistry considerations in the absorber tower (Staudt and Jozewicz, 2003). A saleable fertiliser by-product is produced, avoiding the landfill disposal of FGD waste and offsetting operating costs. There is no adverse effect on fly ash sales since it is pre-collected. The only waste streams are the small quantity of fly ash that escaped the plant’s particulate collection device and is
captured in the wet ESP, and the small volume of adsorbent used to remove mercury from the fertiliser liquid stream.

Water usage is lower than a conventional wet FGD system, and there is no liquid discharge. The largest power consumer is the DBD reactor at around 3% of the plant’s output (Tavoulareas and Jozewicz, 2005). Its power consumption is largely determined by both the amount of NO oxidation needed and the gas flow rate. A higher NOx reduction means higher power consumption. Thus decreasing the NOx concentration in the flue gas by the use of low NOx burners, for instance, would lower the parasitic power consumption. Other power demands include fan power and auxiliary loads for the absorber and fertiliser plants. The ECO® system can be retrofitted into the last fields of an existing ESP or, if there is not enough room, some or all of the components can be built downstream of the ESP. This would reduce the downtime of the plant, but takes up additional space (UNEP, 2010).

A study by Burns & McDonnell concluded that ECO® equipment is at least as reliable as conventional pollution control equipment, predicting better than 99% availability. The ECO® and ECO2® demonstration also showed that they were capable of adapting to power plant conditions, such as load following. Capital and operating costs of the ECO® process are estimated to be around 10–20% lower than a conventional wet FGD + SCR system (Peltier, 2007), partly due to the smaller tower (about two-thirds the size of a limestone wet scrubber) and lower liquid flow rates.

Concern has been expressed that sodium aerosols would foul the electrodes in the DBD reactor, adversely affecting NOx conversion, when high sodium coals are fired. Tests on a slipstream from the Milton R Young Unit 1 near Center, ND, USA, firing high sodium lignite found that although deposits were formed, they were easily removed by washing. Thus the ECO® technology may prove to be viable for these coals, if the ash accumulation can be kept to a minimum (Tolbert and Benson, 2008).

ECO2® has a number of advantages over amine-based reagents also used for CO2 capture. These include a higher CO2 absorption capacity, lower regeneration heat (hence reducing the energy consumption associated with solution regeneration), and lower costs. An assessment by WorleyParsons estimated that the capital and operating costs for retrofitting an ECO2® system on a 220 MWe (net) power plant would be less than 40 US$/tCO2 (captured and compressed), when electrical power costs 50 US$/MWh (Poworspan, 2010). Mills (2012) discusses where research and development are needed that could potentially improve economics and performance of ammonia-based CO2 capture systems. These include development and application of enhanced engineering techniques leading to reduced ammonia slip during absorption and regeneration and vapour losses during operation, improved cooling of the flue gas and absorber to maintain operating temperatures below 10°C (necessary for reducing ammonia slip, achieving high CO2 capacities, and for ammonium carbonate/bicarbonate cycling), and avoiding fouling of heat transfer and other equipment by ammonium bicarbonate deposition as a result of absorber operation with a saturated solution. For more information about the ECO® technologies see http://poworspan.com.

5.4 Comments

The EB-FGT, DBD and PCD technologies are at different stages of commercialisation, with the ECO® system (DBD) being the only one commercially available. EB-FGT generates higher energy electrons externally and then injects them into the flue gas, whereas DBD and PCD generate lower energy electrons within the reactor. DBD and PCD operate at atmospheric pressure, whilst EB-FGT operates under a vacuum. The main parameters for the three technologies are compared in Table 5. Both the EB-FGT and PCD pilot plants inject ammonia into the reactor and remove the resultant ammonium sulphate/nitrate in a downstream particulate collector. On the other hand, ECO® uses three stages, namely a DBD reactor, a downstream ammonia scrubber and a wet ESP. All the technologies can produce a saleable ammonium sulphate/nitrate fertiliser by-product. Although the PCD pilot plant indicates the lowest SO2 and NOx removal efficiency, pilot-scale tests in Korea have

Non-thermal plasma technologies
achieved results comparable to EB-FGT. Elemental mercury is also oxidised in the plasma reactors. ECO® removes over 80% of oxidised mercury, but its removal was not determined in the EB-FGT or PCD pilot plants.

The main drawback of the plasma technologies is the parasitic power consumption, typically up to 3% of total plant production capacity. The power consumption is largely determined by the amount of NOx oxidation required and the flue gas flow rate. Therefore, lowering the NOx concentration in the flue gas by the use of, for example, low NOx burners, could reduce the power consumption. Obradović and others (2011) found that CO emissions increase when flue gas is treated in a DBD reactor, and this may occur in the PCD and EB-FGT systems, as well. Capital and operating costs for the three plasma systems are lower than a conventional SCR + wet FGD system. The operating costs, though, are reliant on the market price for the fertiliser by-product and ammonia.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Comparison of the main parameters of the pilot plants (Pawelec and others, nd)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EB-FGT</td>
</tr>
<tr>
<td>Pilot plant</td>
<td>Kaweczyn power plant, Warsaw, Poland</td>
</tr>
<tr>
<td>Gas flow rate, m³/h</td>
<td>20,000</td>
</tr>
<tr>
<td>Beam or discharge power, kW</td>
<td>50 (x 2 accelerators)</td>
</tr>
<tr>
<td>NOx inlet concentration, ppmv</td>
<td>250</td>
</tr>
<tr>
<td>SO₂ inlet concentration, ppmv</td>
<td>500</td>
</tr>
<tr>
<td>Ammonia stoichiometry</td>
<td>0.8–0.9</td>
</tr>
<tr>
<td>Inlet gas temperature, °C</td>
<td>120</td>
</tr>
<tr>
<td>NOx removal efficiency, %</td>
<td>&gt;75</td>
</tr>
<tr>
<td>SO₂ removal efficiency, %</td>
<td>&gt;95</td>
</tr>
</tbody>
</table>
### 6 Gas phase oxidation

Instead of treating the flue gas by passing it through the plasma reactor (see Chapter 5), ozone (O$_3$) is externally generated in a non-thermal plasma reactor and then injected into the flue gas duct or a NOx reactor. The relatively insoluble NO and NO$_2$ are oxidised into soluble higher oxides, and elemental mercury is oxidised into water-soluble mercury oxide. Oxidation of SOx may also occur. Subsequently the soluble oxides are removed in a downstream system by:

- wet scrubbing, such as Lextran (see Section 6.2), LoTOx™ (see Section 6.3), and NeuStream®-N and NeuStream®-MP (see Section 2.3); or
- condensation, like Eco Power Solutions’ system (see Section 6.1).

A combined denitrification and desulphurisation system is proposed by Bai and others (2012) where reactive oxygen species (O$_3$ and O$_2^+$) produced by ionising oxygen in a DBD reactor are injected into the duct after an ESP or fabric filter. The ozone oxidises NO to NO$_2$ and SO$_2$ to SO$_3$. The NO$_2$ and SO$_3$ are further oxidised to form a fine mist of nitric acid and sulphuric acid by OH radicals generated from the reaction of O$_2^+$ with water in the vapour. The flue gas then passes through a high voltage DC field which collects and condenses the mist as an acidic liquid, a saleable by-product. Around 97% NO and 83% SO$_2$ were removed under the experimental conditions, with an energy consumption rate of 9 Wh/g of NO and 17 Wh/g of SO$_2$ (or 26 Wh/g for combined NO and SO$_2$ removal). A higher SO$_2$ removal rate of 93% could be achieved by decreasing the flue gas inlet temperature from 65°C to 30°C. Mercury reduction was not investigated.

The advantage of ozone injection over the direct oxidation technologies (where the flue gas is passed through the plasma reactor) is a higher NO removal rate (as NO oxidation is more efficient), and at a lower energy consumption. In addition, CO$_2$ does not decompose to CO (Obradović and others, 2011). Nevertheless, ozone generation is expensive due to oxygen demand and high energy consumption. Oxidants, such as hydrogen peroxide, could be used instead of ozone. The Indigo MAPSystem™, developed by Indigo Technologies, includes a hydrogen peroxide stage (Crynack and others, 2009). The technology will not be covered as the Australian company is in administration.

#### 6.1 Eco Power Solutions’ system

Eco Power Solutions’ (EPS) Multi-Pollutant Air Quality Control System (MP-AQCS Reactor Module™), formerly called COMPLY 2000®, concurrently removes NOx, SOx, CO$_2$, mercury, other heavy metals, particulate matter and unburnt hydrocarbons via oxidation and condensation. It has been included on the shortlist of technologies that offer the potential of reduced compliance costs and improved overall performance by the US EPA in its preliminary MATS ruling (Crapsay, 2012a). The system has been tested on the 1.5 MW coal- and 2 MW natural gas-fired pilot plant at the Eco Power Technology Center in Louisville, KY, USA. Removal levels of 99% SOx, 98% NOx, 95% mercury, 99% particulate matter (PM$_{2.5}$ and PM$_{10}$), 99% halogens, 99% heavy metals (including arsenic, cadmium and chromium), and 30% CO$_2$ have been achieved (Crapsay, 2012b). Over 90% of CO$_2$ (with a purity of >90%) is removed when the additional CO$_2$ Capture Module is fitted (Crapsay, 2013). Saleable by-products can be produced.

The core of the EPS system is the Reactor Module where most of the chemical reactions and the process of condensation and subsequent removal takes place. The Reactor Module is installed downstream of the ESP or fabric filter. Ozone is injected into the duct (see Figure 15) upstream of the Reactor Module to allow sufficient residence time for the oxidation of nitric oxide to water soluble NO$_2$. As the flue gas enters the Reactor Module, a mixture of hydrogen peroxide (2% concentration) and water is injected through an array of high pressure nozzles (called first stage foggers) to create a fine water mist. Sulphur dioxide and sulphur trioxide are converted into sulphuric acid, and elemental...
mercury into water soluble mercury oxides. The water also helps to oxidise NO₂ into nitric acid, CO₂ into carbonic acid and the halogens into hydrochloric, hydrofluoric and hydrobromic acids. Additionally, water helps provide adiabatic cooling of the flue gas. Sulphuric acid begins to condense out first as it has the relatively higher dew point temperature. Subsequent cooling is provided through a second fogging stage, where only water is injected. The flue gas then passes through packing material that provides contact surface to enable completion of the chemical reactions and scrubbing to facilitate the condensation process. This ensures that any remaining acids, heavy metals and particulates are removed. The condensate, which contains the acids, particulates and heavy metals, collects at the bottom of the unit as wastewater. Finally, the flue gas passes through mist eliminators to prevent water droplet carryover that can damage downstream equipment, and an activated carbon filter, which acts as a polishing unit.

The collected acidic wastewater requires neutralisation with limestone, quick lime or caustic soda (sodium hydroxide). Caustic soda has the advantage in that it can neutralise carbonic acid, but the major disadvantage is its high cost. Limestone is inexpensive but it cannot neutralise carbonic acid, and it also produces CO₂ via chemical reactions with nitric and sulphuric acids. The salts from the neutralisation process can be converted into by-products or sent to landfill for disposal. The treated water can be reused in the foggers (Littleford and Jolly, 2010a,b).

The EPS system is capable of removing over 95% of all current regulated pollutants in one process vessel. In the upgraded version, a CO₂ capture rate of over 90% can be achieved by controlling the water flow and gas velocity in the additional CO₂ Capture Module. The CO₂ Capture Module can be fitted independently on power plants with existing pollution control systems. Ozone emission is not a concern because the activated carbon filter captures any unreacted ozone. The EPS system injects ~8.3 L/min of water per MW through the foggers (Crapsey and Jolly, 2012). Water consumption is lowered by recycling 50–60% of the water. Some make-up water, though, is still required. Parasitic power consumption is around 1% if NOx is not recovered, increasing to 4–7% with NOx removal, due to the power consumption of the ozone generator (Crapsey and Jolly, 2012). A 200 MW unit is predicted to consume some 800–1400 kW/h, including the power consumed by the fans to overcome
the additional pressure drop imposed by the system (Crapsey, 2013). If existing fans cannot be upgraded, booster fans may be required (Eco Power Solutions, 2012).

The capital costs of an EPS system are lower than conventional pollution control technologies removing SO2, NOx and mercury. Capital expenditure (CapEx) varies between 380 and 600 US$/kW compared to 600–900 US$/kW for conventional SCR, FGD plus activated carbon injection systems. On average, the operating expenditure (OpEx) is comparable to the conventional technologies, a result verified by EPRI in their evaluation of the EPS system (Crapsey, 2012b, 2013). Since the system is installed downstream of the ESP or fabric filter, the quality of the collected fly ash is unaffected and can still be sold. Furthermore, saleable by-products can be produced from the condensate. The captured CO2 has a purity of over 90% and can be sold for applications such as enhanced oil recovery, or can be converted to marketable ethanol through EPS’ patented process (Crapsey, 2013). The smaller footprint of the EPS system makes it relatively easier to retrofit. Its modular construction means that it can be sized for all boiler sizes. Each 25 MW module treats a 28.3 m³/s flue gas flow rate. More information about the EPS system can be found on the www.ecopowersolutions.com website.

6.2 Lextran technology

Lextran Ltd, based in Israel, has developed a regenerative, catalytic wet scrubbing process that simultaneously removes SOx and NOx from flue gas. Installations include small boilers (20–25 MW) in China and Romania, and a sintering plant installation (300 MWe equivalent) at a Chinese steel plant. A test facility using a slipstream from Israel Electric Corporation’s 2600 MW coal-fired Orot Rabin power plant is being run to provide statistical analyses on the performance and testing ground of the Lextran technology (Udasin, 2012). The system removes 99% SOx and up to 90% of inlet NOx (Davidor, 2013), and a saleable by-product is produced.

After exiting the particulate control device, ozone is injected into the dedusted flue gas to oxidise NO to NO2 (see Figure 16). The flue gas then enters the counter-flow wet scrubber where a proprietary organic catalyst in a water emulsion is sprayed. The proprietary organic liquid catalyst contains an active sulphur-oxygen functional group that enhances the oxidation reactions of SOx and NOx into SO4²⁻ and NO3⁻ anions. After facilitating the initial oxidation, the catalyst is released back into the

![Figure 16 Lextran process](Geven, 2013)
process to oxidise more SOx and NOx. The anions are neutralised with a basic reagent, such as aqueous ammonia (ammonium hydroxide) or potassium hydroxide, to form sulphate and nitrate salts. The cleaned flue gas then passes through the mist eliminators to remove entrained droplets, and is emitted to the atmosphere through the stack.

The liquid at the bottom of the scrubber is recirculated to the spray nozzles. A bleed stream from the recirculation loop is filtered to remove the particulate matter that escaped capture in the upstream particulate control device, before it passes into the decanter. Here the liquid separates into two phases. The upper organic (catalyst) phase is returned to the scrubber for recirculation. The lower aqueous phase containing the sulphate and nitrate salts can be sold as a fertiliser.

The Lextran technology can remove SOx and NOx in one single pass to meet current pollution regulations. Some heavy metals, such as mercury, can also be removed (Davidor, 2011). The process is a closed-loop system that produces no liquid wastes, and so no water treatment facilities are required. The only solid waste for disposal is the filter cake containing the particulate matter. The lifetime for the catalyst is not limited but needs to be replenished every four to five years due to some losses (Geven, 2013).

Conventional open spray wet scrubber systems can be easily retrofitted to employ the Lextran solution. No extensive infrastructure changes are required as the existing spray tower only needs some reconstruction of the internal liquid transportation systems, and some of the existing systems or auxiliary installations can be utilised (Lextran, 2012). The Lextran system also has a smaller footprint than a conventional wet FGD + SCR system. According to Lextran, its technology is 20–40% cheaper to construct and saves 20–50% in operating costs compared to separate conventional pollutant collection systems (Lextran, 2012). This is without the revenue from the sale of the by-product fertiliser. The type of fertiliser produced can be controlled by the choice of reagent (such as ammonium hydroxide or potassium hydroxide) for neutralising the sulphuric and nitric acids. A niche market is its application to small boilers (20–150 MW) where limestone wet scrubbers are too expensive and other solutions, such as dry scrubbing, are not efficient enough (Geven, 2013). The technology, though, is easily scalable to large boilers. More information about the technology can be found on Lextran’s website (www.lextran.co.il).

### 6.3 LoTOx™ system

The LoTOx™ system (based on Cannon Technology’s patented Low Temperature Oxidation (LTO) process for the removal of NOx emissions), was developed by BOC Gases, now part of the Linde Group. It involves injecting ozone into the flue gas to oxidise NOx and mercury into water soluble oxides, which are subsequently removed, along with SO2 and HCl, in a wet FGD scrubber. A small-scale demonstration of LoTOx™, combined with the FGD Rapid Absorption Process (RJM-Beaumont™), was carried out at three 25 MW coal-fired power boilers at the Medical College of Ohio, USA. NOx removal rates of 90–95% and >95% SO2 were achieved (Jarvis and others, 2003). Mercury reduction was not measured. The current focus for LoTOx™ is for use in petroleum refineries.

Ozone is generated on-site and on demand by passing industrial-grade oxygen through a non-thermal plasma reactor, described as a ‘corona discharge’ reactor, in response to the amount of NOx present in the flue gas. It is then injected into the flue gas (at a temperature below 150°C), either in a separate reactor (see Figure 17) or into the flue gas duct, upstream of a wet FGD scrubber and after the particulate control device. The ozone reacts with NO and NO2 to produce higher oxides, such as N2O5. These react with the water vapour in the flue gas to form nitric acid. Elemental mercury is oxidised to soluble HgO. The nitrogen and mercury oxides, nitric acid, SO2 and HCl, plus any residual ozone, are then removed in the wet scrubber.
Theoretically, SO\textsubscript{2} could potentially be oxidised to SO\textsubscript{3}, which is not significantly captured in limestone wet scrubbers, and CO to CO\textsubscript{2}. However, field tests have shown that the reaction rates are much slower compared to the predominant NO\textsubscript{x} and mercury reactions; significant oxidation of SO\textsubscript{2} and CO does not occur at the designed residence time (BOC Process Gas Solutions, 2004; Jarvis and others, 2003). In fact LoTOx\textsuperscript{TM} is claimed to enhance SO\textsubscript{2} removal efficiency by ~5%. The choice of wet scrubber (lime, limestone, ammonia) does not affect the performance of the LoTOx\textsuperscript{TM} process because the solubility of N\textsubscript{2}O\textsubscript{5} is significantly higher than that of SO\textsubscript{2} (Tavoulareas and Jozewicz, 2005). Nevertheless, in calcium-based systems, absorption of N\textsubscript{2}O\textsubscript{5} results in the accumulation of highly soluble calcium nitrate in the scrubbing liquor. The calcium nitrate could possibly be recovered and used as a speciality fertiliser. In an ammonia-based FGD system, designed to produce a salable ammonium sulphate fertiliser by-product, the ammonium nitrate produced by LoTOx\textsuperscript{TM} adds to the value of the by-product (Jarvis and others, 2003).

Removal efficiencies of ~95% for SO\textsubscript{2}, 70–95% for NO\textsubscript{x} and 50–94% for mercury have been achieved in bench-scale tests, and pilot- and small-scale (25 MW) demonstrations, depending on the coal rank, residence time, operating temperature, and stoichiometric ratio of O\textsubscript{3}:NO\textsubscript{x} (BOC Process Gas Solutions, 2004; Jarvis and others, 2003; Omar, 2008; UNEP, 2010). Tests at Western Research Institute’s combustion test facility removed over 90% of NO\textsubscript{x} and over 80% of elemental mercury at an O\textsubscript{3}:NO\textsubscript{x} ratio of less than 2 (Omar, 2008). In most of the cases, a lower reactor temperature is preferred over a higher temperature due to ozone dissociation. However, the combination of both low residence time and high temperature was effective in the oxidation of both NO\textsubscript{x} and elemental mercury. A higher residence time, lower temperature, and higher O\textsubscript{3}:NO\textsubscript{x} ratios contributed to the highest NO\textsubscript{x} and elemental mercury reductions. Generally, a higher NO\textsubscript{x} reduction is achieved for a subbituminous coal compared to a bituminous coal at similar operating conditions. Table 6 shows how the addition of LoTOx\textsuperscript{TM} is expected to enhance mercury removal for all coals, especially subbituminous coal and lignite.

Installation of LoTOx\textsuperscript{TM} by itself for control of NO\textsubscript{x} emissions is normally recommended when inlet NO\textsubscript{x} concentration is below 130 g/GJ (0.3 lb/MMBtu). Above this value, a LoTOx\textsuperscript{TM} installation is required.

**Table 6** Projected mercury levels with and without ozone injection (Jarvis and others, 2003)

<table>
<thead>
<tr>
<th>Coal type</th>
<th>Typical Hg\textsuperscript{a} as % of total Hg</th>
<th>Hg removal with FGD alone</th>
<th>Hg removal with LoTOx\textsuperscript{TM} and FGD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous</td>
<td>70–85</td>
<td>76</td>
<td>94</td>
</tr>
<tr>
<td>Subbituminous</td>
<td>15–45</td>
<td>33</td>
<td>92</td>
</tr>
<tr>
<td>Lignite</td>
<td>10–30</td>
<td>19</td>
<td>91</td>
</tr>
</tbody>
</table>

FGD system is a limestone forced oxidation wet scrubber.

Figure 17 Schematic diagram of LoTOx\textsuperscript{TM} system (UNEP, 2010)
recommended as part of an integrated control approach operating in series with an alternate control process that is capable of moderate NOx removal, such as a low NOx burner (Tavoulareas and Jozewicz, 2005; UNEP, 2010). By combining the two technologies, users may be able to avoid installing a SCR system, which is expected to have higher capital and operating costs than LoTOx™. Generally, SCR will be more cost effective in applications with higher inlet NOx concentrations whereas LoTOx™ is more cost effective in applications with lower inlet NOx levels. Ozone generation forms the highest part of the operating costs of LoTOx™ due to its oxygen demand and high power consumption.

A LoTOx™ system has good load-following capability, is easy to retrofit with its small footprint, has relatively low capital costs, and has no adverse impact on boiler operation (Jarvis and others, 2003). The high auxiliary power consumption from the multiple ozone generators required to produce the ozone for the process in a utility-scale plant is a drawback. It is significantly higher than the power consumption from an SCR. The auxiliary power requirement for a 500 MW plant is projected to be 5–12.5 MW or 1–2.5% of the gross power output (Tavoulareas and Jozewicz, 2005). In addition, cooling water is required, around 17,034 L/min for a 500 MW plant (assuming it is available at 21°C). No ozone slip is predicted as any residual ozone in the oxidised flue gas is readily absorbed into the aqueous scrubber medium. Whether a wastewater treatment plant is required and the amount of waste products for disposal is dependent on the wet scrubber technology used. Limestone wet scrubbers are discussed in Section 2.1, and the non-calcium desulphurisation technologies are reviewed in Zhu (2010). Several petroleum refineries have demonstrated the performance and reliability of LoTOx™, but the technology has yet to be demonstrated at a utility-scale coal-fired plant.

6.4 Comments

The EPS system, Lextran and LoTOx™ processes are at different stages of commercialisation. LoTOx™ technology has been around for the longest time, with several systems installed at petroleum refineries. Lextran has only recently installed its system at a large-scale Chinese steel plant (sintering machine), although it has been installed on several small-scale boilers. The EPS system has only been tested at pilot scale. None of the technologies has yet been demonstrated at full scale on a coal-fired power plant. The processes have similar removal efficiencies for SO2 and NOx, and all remove some mercury (over 90% in the EPS and LoTOx™ technologies). The EPS system additionally removes 30% to over 90% of the CO2. All of the processes can produce saleable by-products (fertilisers), although in the case of LoTOx™, it depends on the applied wet scrubber technology. The footprint of the three technologies is smaller than a conventional wet FGD + SCR system, and the capital costs are expected to be lower. Moreover, operating costs should be lower, especially if there is a local market for the by-products. The quality of the fly ash is unaffected since all three systems are installed after the particulate control device. This allows the fly ash to be sold, further reducing operating costs.

The main drawback of all the technologies is their high auxiliary power consumption mainly due to the on-site ozone generators. Parasitic power generation can reach ~3–4% of total plant output. Lowering the amount of NOx in the flue gas before the ozone injection point by the use of low NOx burners, for example, would lower power consumption.
7 Others

This chapter discusses three technologies, namely Shell Cansolv® (an amine-based scrubbing process), CEFCO (a ‘free jet collision scrubbing’ system) and CSNOx (which employs ultra-low frequency wave technology).

7.1 Shell Cansolv® technology

Cansolv Technologies (a wholly-owned subsidiary of Shell Global Solutions International) has developed an integrated SO₂-CO₂ system which sequentially scrubs SO₂ and CO₂ from flue gas using proprietary regenerable aqueous amine-based solvents. The SO₂ component is employed commercially on 14 units at oil refineries, chemical plants, non-ferrous smelters and other industrial plants; more are in the engineering, procurement or construction phase (Stéphenne and others, 2012). It is currently being installed on a new 1200 MW coal-fired power plant being built by China Guodian Corp at Duyun, China, where over 99.9% of SO₂ will be removed from the flue gas. The CO₂ component has only been tested at pilot scale, including a test at SaskPower’s Popular River coal-fired power plant, Canada, in 2006. Operations have started on an integrated SO₂-CO₂ pilot plant at RWE npower’s Aberthaw power station in South Wales, UK. It is designed to capture 50 tCO₂/d, which is about the amount produced by 3 MW of electricity generation (Carbon Capture Journal, 2013). The first commercial application of the SO₂-CO₂ Shell Cansolv® technology is under construction at the SaskPower’s lignite-fired Boundary Dam 150 MW Unit 3 in Estevan, Saskatchewan, Canada. SO₂ emissions will be essentially zero, since residual SO₂ is captured in the CO₂ unit, and 90% of CO₂ will be removed (~1 MtCO₂/y). Start-up is due at the end of 2013 (Shaw, 2012).

The Shell Cansolv® system (see Figure 18) is installed downstream of the particulate control device. The dedusted flue gas is first sent to the SO₂ absorber, then on to the CO₂ absorber, before it is emitted to the atmosphere through the stack. The flue gas is first quenched and cooled to 30–60°C in the prescrubber section, which also removes residual particulates and is located at the bottom of the SO₂ absorber. SO₂ and CO₂ are absorbed, in turn, from the gas by contact with the Shell Cansolv® solvent through sections of structured mass transfer packing in the absorption towers. Lean cool amine is fed to the top of each tower, where the pollutant is absorbed into the amine as the absorbents flow down the column (counter current to the feed gas). The rich (pollutant laden) amine collects in the sump of the absorber tower and is pumped to the applicable stripper for regeneration. As the absorption of CO₂ is an exothermic reaction, inter-stage cooling is employed to remove this heat from the absorber tower, thus maintaining absorption efficiency.

The rich amine absorbent is pumped to the appropriate regeneration tower through a lean/rich heat exchanger that recovers sensible heat from the lean amine. A reboiler uses low pressure steam to indirectly generate stripping steam which is injected into the bottom of the column. As the liquid solution flows down the tower, it meets the rising hot steam in sections of mass transfer packing where the heat reverses the absorption reaction and returns the SO₂ and CO₂ to the gas phase. In each case, the gaseous product is carried out of the top of the tower and cooled in the respective stripper condensers where most of the steam condenses. Water-saturated product and product-saturated condensate are separated in the stripper overhead accumulator and the condensate is returned to the top of the stripper tower as reflux. The gaseous product leaves the stripper overhead accumulator and is delivered at positive pressure for downstream handling.

The regenerated amine exits the stripper and passes first through the lean/rich amine heat exchanger and then through a second cooling unit. The cooler the solvent, the better its performance. A portion of the lean amine is treated in the amine purification unit to prevent accumulation of heat stable salts.
formed from strong acids in the flue gas that would degrade the amine solvent. After treatment, all of the lean amine is sent back to the top of the absorption tower.

This is one of the most efficient SO₂ capture technologies, removing over 99.9% in the SO₂ absorption tower and the rest in the CO₂ absorption tower, resulting in 100% removal. However, only ~50% of SO₃ is captured and therefore a SO₃ removal system may be required to meet strict SO₃ emission regulations. Since NOx adversely affects the performance of amines, a power plant will need to have a NOx control system fitted.

A number of heat recovery features can be incorporated to reduce energy consumption and lower
operating costs. Heat recovery in the lean/rich amine heat exchangers reduces both the amount of steam necessary to regenerate the solvent and the amount of cooling water required to cool the lean solution to absorber conditions. The largest operating cost in an amine-based CO₂ capture unit in a coal-fired power plant is the energy required for solvent regeneration. One option for recovering energy is a mechanical vapour recompression (MVR) system, which recovers latent energy from the lean amine exiting the CO₂ stripper and reintroduces it into the system via the reboiler. This lowers fresh steam consumption by some 30%. Taking into account the energy consumption of the compressor, it is estimated that the energy demand improves by ~15%. Latent heat can also be recovered from the SO₂ stripper overhead stream through MVR. (The CO₂ stripper overheads are unsuitable for heat recovery.) The recovered energy is being recycled at the Boundary Dam plant to reduce the primary low pressure steam requirement for CO₂ capture. It is estimated that up to 15% of the energy requirements in the CO₂ capture system can be obtained from the desulphurisation system. Heat can also be recovered from the exothermic reactions when the SO₂ by-product is converted into sulphuric acid. Around 1.7 t of steam/t acid can be produced. This energy can be sent to the CO₂ regenerator, reducing the net energy demand of the CO₂ process and to further offset CO₂ capture costs (Shaw, 2009, 2012). Adding the SO₂-CO₂ system, with integrated heat recovery and CO₂ compression, is expected to reduce the power output of the refurbished 150 MW Boundary Dam Unit 3 to 110 MW (Modern Power Systems, 2012). The tail gas from the sulphuric acid plant can be treated in a secondary smaller absorber or mixed with the power plant flue gas for treatment in the main Shell Cansolv® system to control SO₂ emissions from the acid plant.

Water consumption is claimed to be low primarily because it is a regenerable system. However, significant amounts of water are consumed in the cooling systems for the flue gas (prescrubber) and amine. Water consumption is site-specific. In one case study, it was found that a Shell Cansolv® CO₂ capture unit would consume around 53 litres of process water/tCO₂, 24.5 L of demineralised water/tCO₂ and 28 m³ cooling water/tCO₂. Low pressure steam usage would be 1.18 t/tCO₂ (Just and Shaw, 2008). Liquid effluents are minimal. At the Boundary Dam plant, the towers are designed as rectangular vessels, rather than the typical cylindrical tower design. This allows a common wall to be shared between the SO₂ and CO₂ sections, reducing the footprint (Shaw, 2012). Saleable by-products can be produced, offsetting operating costs. At the Boundary Dam power plant, sulphuric acid (for fertilisers) will be produced from the high purity SO₂ product, and the CO₂ (>99.9% pure) will be used for enhanced oil recovery. It is also planned to inject a portion of the CO₂ into a deep saline aquifer as part of the Aquistore project (Modern Power Systems, 2012). The quality of the fly ash, and hence its saleability, is unaffected since the Shell Cansolv® system is installed downstream of the particulate control device.

New amine solvents are being developed to improve performance. Tests suggest that the new CO₂ absorbent DC-201 has better CO₂ loading capacity, lower heat of reaction, lower amine regeneration energy and lower cooling requirements than the existing absorbent DC-103. The increased CO₂ loading capacity leads to a reduction in liquid circulation rate, and a lower contribution of the sensible heat and latent heat components in the regenerator. Amine regeneration energy savings of ~20% (compared to DC 103) are expected (Stéphenne and others, 2012). These features should help reduce both capital and operating costs. More information about the technologies can be found on Cansolv Technologies Inc’s website (www.cansolv.com).

### 7.2 CEFCO process

The CEFCO (Clean Energy and Fuel Company) process sequentially removes trace metals (including mercury) and fine particulates (including PM₁₀), SOₓ, NOₓ and CO₂ in a series of four reactor modules. Each module consists of two components: the capture of the targeted pollutant and its conversion into a saleable product. The first component uses Ewan’s shockwave ‘free jet collision scrubbing’, a process utilised at US nuclear waste and EPA Superfund Cleanup incineration facilities to control hazardous waste emissions in the US government’s ‘zero emissions’ programme. The
second component (the ‘Cooper process’) employs chemical reagents to convert the captured pollutant into the required end product. Saleable trace metals, potassium sulphate and nitrate fertilisers, and pure CO₂ or alkaline bicarbonate (which can be used to make baking powder) are produced. Removal efficiencies of over 99.99% for mercury, fine particulates, SOx and NOx, and 99% of CO₂ are claimed. The process has been successfully tested at a pilot plant (1–3 MWh) at the Peerless Manufacturing Company’s industrial facility in Wichita Falls, TX, USA (Tang and Sanyal, 2012a,b). In 2012, a sour gas treatment speciality engineering company in the USA became a CEFCO sub-licensee. A front end engineering design study is currently being carried out to bring the CEFCO technology to BASF Corporation’s Freeport facilities, TX, USA (Tang, 2013). Chemical products from the captured emissions at the chemical incineration plants will be used as a chemical feedstock source. This forms part of BASF’s Verbund integration concept of adding value through efficient use of resources.

The CEFCO modules are installed downstream of the ESP/fabric filter. The flue gas (see Figure 19) enters the top of the aerodynamic reactor where steam is injected through supersonic injector nozzles to generate shockwaves. These shockwaves perform two functions. Firstly, their collisions of molecules energise the targeted pollutant to react with the reagent injected into this supersonic region. An innovative feature of the process is the transfer of energy (heat and pressure) resulting from the Mach speed collision impacts, without any external heating. Secondly, the collisions shatter the reagent droplets into very small (µm) droplets, which rapidly react with the targeted pollutant molecules. The reaction products are encapsulated by steam condensation within the droplets. The droplets, along with the surrounding gaseous stream, are then accelerated (the shockwaves act as the motive force) through in-line subsonic nozzles. These cause the gaseous stream to expand rapidly into a sub-atmospheric zone, allowing the small droplets to grow in size through repeated collisions, nucleation, agglomeration and moisture condensation. The ‘free jet expansion’ changes the temperature and pressure environment of the product molecules and, in the conditions created, there is no possibility of reaction reversal. The droplets containing the reaction products and reagents are stripped from the flue gas in the aero-coalescer (gas/liquid separator) and the resultant liquid (together with vapour condensation) is sent to the product tanks for processing into saleable products. The flue gas then passes into the second module to remove the next pollutant, in a similar way. The flue gas takes just seconds to pass through each module (Tang, 2011; Tang and Sanyal, 2011).

Figure 19  CEFCO process (Tang, 2011)
The selectivity of the reagent for capturing the required pollutant is maintained by manipulating the residence time, velocity, temperature, pressure and pH in each reactor module. Typically, a hydroxide solution (KOH or NaOH) and/or a carbonate solution (K₂CO₃ or Na₂CO₃) is used as the reagent, enabling saleable products to be made.

The process utilises a slipstream of the ‘waste steam’ (or ‘low quality steam’) leaving the last turbine that is sent to the condenser. Between 3 and 6 wt% of steam at a pressure between 0.69–2.76 MPa is required to generate the shockwaves (Tang, 2011, 2012). If steam is unavailable, then compressed air can be used to produce the shockwaves as a low cost substitute. A further amount of steam (heat source) is used to remove the CO₂ from the aero-coalescer liquids in a decarbonation tank at over 100°C.

Water conservation is optimised, and with water vapour condensation and water recovery, the CEFCO process is a net generator of water. Hence the steam required to generate the shockwaves can be regarded as ‘borrowed water’. A material balance carried out for a 1000 MW power plant employing all four modules estimated that 3886 t/MWe, 2941 t/MWe and 2819 t/MWe of water would be produced when burning US lignite, subbituminous and high sulphur bituminous coals, respectively. The energy penalty (parasitic load) would be 22.8%, 12.4% and 13% for the lignite, subbituminous and bituminous coals, respectively (Tang, 2012). These values do not take into account the energy required for CO₂ compression and transportation. The parasitic load could be excessive for plants firing lignite. Instead of CO₂ compression, the captured CO₂ could be retained in its solid form (potassium or sodium bicarbonate) for easier shipment to the end user, thus avoiding the compression costs. Gaseous CO₂ is then liberated at the end user’s site by heating in a decarbonation tank (at >100°C). The potassium/sodium carbonate liquid generated in the decarbonation process could be returned to the CEFCO plant for reuse in the process.

CEFCO is designed as a modular process. The modular unit can handle flue gas emissions of 25, 50, 100 and 200 MW equivalents. The units can be stacked, as required, to fit in a limited footprint. In addition, the reactor modules can be independently installed, for instance, fitting the sulphur reactor module (SRS) to reduce SOx emissions. CEFCO has a small footprint; the sulphur reactor system (SRS) is smaller than a conventional wet FGD system, and so is more easily retrofitted. CEFCO utilises a recirculating and regenerative reagent system to minimise the use of reagents (such as potassium carbonate). However, this does add to the complexity of the process. The CapEx cost for a 1000 MW plant (with all four modules) is US$800 million, whilst OpEx costs for firing moderate sulphur North Dakota lignite, low sulphur PRB subbituminous and high sulphur bituminous coals are estimated to be around US$582 million, US$269 million and US$1121 million, respectively, when manufacturing potassium-based saleable by-products. Revenue generated from the sale of the by-products will reduce the OpEx costs. Pre-collection of the fly ash means that it can also be sold. If the process is operated in a ‘capture-only’ mode for environmental compliance, without the production of saleable products, then the reagent component of the OpEx costs can be reduced by using cheaper sodium- or calcium-based reagents instead of potassium-based ones. For example, the projections provided to the US Department of Energy, Fossil Fuel Office in June 2012 indicated that in a ‘capture-only’ mode, the annual overall OpEx costs would be reduced to around US$255 million, US$140 million and US$235 million for lignite, subbituminous and high sulphur bituminous coals, respectively, when using a sodium hydroxide reagent (Tang, 2013). More information about the process can be found on CEFCO’s website (www.cefcoglobal.com).

7.3 CSNOx process

Ecospec Global Technology Pte Ltd, based in Singapore, has developed the CSNOx process that uses seawater or freshwater treated in a patented ultra-low frequency wave system to simultaneously remove SO₂, NOx and CO₂ from flue gas. Two cheaper, trimmed versions of CSNOx are available. The cSOx process removes SO₂ and enough CO₂ (5%) so that a net carbon neutral position can be
achieved (Chew, 2013). The CNOx system removes CO₂ and NOx. Although the technologies are applicable to power stations and other industrial plants, they have been initially targeted at the shipping industry. In data verified by the American Bureau of Shipping, CSNOx captured 99% of SO₂, 66% of NOx and 77% of CO₂ from the exhaust of a 11 MW heavy oil diesel engine (50% gas load) on a tanker (Chew, 2010). Other tests have achieved higher NO₂ removal rates of over 80%. In 2012, Sembawang Shipyard, a wholly-owned subsidiary of Sembcorp Marine, invested S$10 million, giving the shipyard a 20% equity interest in Ecospec Global Technology.

Figure 20  CSNOx process configurations (Ecospec Global Technology, nd)
The CSNOx process can be operated as an open loop system (see Figure 20a) for locations where water supply is abundant, such as power plants on the coast or ships on the open sea. For on-shore plants with limited water supply, the closed loop version, which does not produce any wastewater, can be employed. The closed loop system (see Figure 20b) consists of two separate water treatment systems, Stages 1 and 2. In Stage 1, water passes through the ultra-low frequency energising system (ULFES) treatment tank and then the SO₂ absorption enhancer (SAE, which treats the water with time varying ultra-low frequency electromagnetic waves), before the energised and reactive water is sprayed into the lower two levels of the abator tower. The spray pattern created with the upward flowing flue gas breaks down the SO₂ into elemental sulphur and oxygen. Stage 2 water goes through another ULFES tank and then the CO₂ and NOx reducers (CNR) to improve the removal ability of the water. The energised water is sprayed into the upper three levels of the abator tower, where NOx and CO₂ in the sulphur-free flue gas are principally reduced to their respective elemental states (nitrogen and carbon) and oxygen. An ESP can be installed to collect the carbon particles or another stage can be included in the tower to wash the carbon particles out of the cleaned flue gas with natural water. The wash water from the various levels is sent to their respective ULFES tanks for retreatment and recirculation (Chew, 2010, 2012; Ecospec Global Technology, nd).

The CSNOx process is capable of removing SO₂, NOx and CO₂ in a single system without producing secondary pollutants or generating further CO₂ emissions. Sulphur, nitrogen, carbon particles and oxygen are produced. Elemental sulphur and carbon particles are removed in the side stream filtration systems from the ULFES tanks. The recovered carbon particles can be combusted in the boiler, generating additional electricity. The wash water has a low concentration of nitrates and nitrites (<3 ppm), carbonates, bicarbonates and sulphates, and therefore, in the open system mode, can be discharged without any treatment. In the closed loop mode, a small amount of water will need to be bled to prevent the build-up of nitrates, nitrites and other compounds in the water.

Capital costs for CSNOx are around 300 US$/kW. Operating costs are low as the process requires no chemicals or heat energy. Parasitic power consumption is estimated to be 100–300 kW, based on a 11 MW diesel engine exhaust gas marine application with an exhaust gas flow of 100,000 m³/h, that is, about 1–2.7% (Chew, 2010). The compact size of CSNOx means that it could be more easily retrofitted in power plants. However, none of the three processes (CSNOx, cSOx or CNOx) have yet been tested on a slipstream from a coal-fired power plant. CSNOx, though, has been retrofitted onto a bulk carrier and a cruise ship where heavy oil fuels are combusted. For large-scale plants, additional modules in stages 1 and 2 are needed, the number depending on the gas and pollutant loads, and reduction efficiency required. In addition, CSNOx has not been proven for boilers operating at a variable load. More information about the process is available on the company’s website at www.ecospec.com.
8 Conclusions

A host of new environmental regulations are being introduced that will tighten existing limits on emissions from coal-fired power plants and introduce restrictions on previously unregulated pollutants. Multi-pollutant technologies, which remove two or more pollutants in a single system, have been developed that will be able to achieve the new emissions limits at a potentially lower cost than a series of traditional single pollutant control systems that remove the same number of pollutants.

The multi-pollutant processes are summarised in Table 7. The majority of the processes are at the commercial or near-commercial stage. The mercury removal efficiency of limestone wet scrubbers, which were developed for SO₂ removal, can be enhanced by increasing the amount of oxidised mercury in the flue gas and preventing mercury re-emission. The Airborne Process™, NeuStream®-MP and SkyMine® all have high SO₂, NOx and mercury removal efficiencies and, in the latter two processes, additional capture of CO₂. SkyMine® captures CO₂ as a solid product, therefore avoiding the cost of CO₂ compression. All of these wet scrubbing processes can produce saleable by-products, although sales may be limited by proximity to the end market and the availability of cheap transport. The main drawback of the wet scrubbing systems is their high water consumption and the volume of wastewater that requires treatment. The Airborne Process™, NeuStream®-MP and SkyMine® technologies consume less water than limestone wet scrubbers. Moreover, they do not increase power plant CO₂ emissions, unlike limestone wet scrubbers where CO₂ is generated in the desulphurisation process.

The semi-dry scrubbing systems, namely spray dry scrubbers (SDSs) and circulating dry scrubbers (CDSs), have high SO₂, SO₃ and oxidised mercury removal efficiencies. For some coals, mercury removal may entail the utilisation of a mercury sorbent. Oxidising NO, the chief component of NOx, into water soluble higher nitrogen oxides would enable its removal in a SDS or CDS. This is accomplished in the VersaMAPSTM system, which combines a NO oxidiser with multiple CDSs. But the technology has only been applied to small-scale boilers and industrial plants.

SDSs are typically used at power plants burning low to medium sulphur coals, whilst CDSs can be applied to units burning low to high sulphur coals. Both systems have a good turndown capability, and similar capital costs, water usage and power consumption. They also have the advantages over limestone wet scrubbers of lower investment costs (than a similar sized wet scrubber), lower water demand (~60–70%), lower parasitic power consumption, no production of wastewater, dry by-products, and a smaller footprint (which may be easier for retrofit applications). However, operating costs are generally higher than those for limestone wet scrubbers mainly due to the higher sorbent costs. Multiple absorber vessels are required for units with a capacity higher than about 400 MW, although some CDS designs are now available in single unit sizes of 750 MW.

Both ReACT™ and SNOX™ are dry, regenerable processes removing SO₂, SO₃ and NOx, and act as a polishing device for particulates. Although ReACT™ has a lower NOx removal efficiency than SNOX™, it does capture mercury (both elemental and oxidised). Since they are dry systems, they consume little or no water, and require no wastewater treatment systems. ReACT™ is better suited for low to medium sulphur coals, as the amount of activated coke required for high sulphur coals increases substantially, resulting in the need for additional adsorber and regenerator modules, and supplementary solids conveying equipment. On the other hand, SNOX™ is only economically attractive for plants firing high sulphur coals (it was designed for high sulphur fuels). Parasitic power consumption of ReACT™ is about 0.7%, whereas there is a potential net power gain with SNOX™ on large units (≥500 MW) due to its heat recovery features. Operating costs for ReACT™ could be reduced if cheaper and more efficient activated carbon sorbents were developed.

Catalytic ceramic filters, Max-9™ and TOXECOM™ technologies can remove particulate matter and
mercury (with upstream injection of mercury sorbents) and, in the case of catalytic ceramic filters, NOx as well. Injecting trona can additionally capture SO2, but often at the expense of increased consumption of the mercury sorbent in order to maintain a high mercury removal efficiency. Typically, catalytic ceramic filters would be installed between the economiser and air heater due to the higher flue gas temperature required for the NOx reduction reactions. However, catalytic ceramic filters have not yet been demonstrated on large-scale coal-fired power plants, and there is a risk of filter breakages. Moreover, the fly ash cannot be sold to the concrete industry as it is contaminated with spent and unused sorbents, unless it is installed after an ESP or fabric filter (as is the case with Max-9™). Loss of ash sales means a loss in revenue and additional disposal costs for the power plant owner. TOXECON™ has the advantage of pre-collecting around 99% of the fly ash, whilst TOXECON-II™ pre-collects about 90%, enabling the majority of fly ash to be sold. Non-carbon based sorbents and ‘concrete compatible’ carbon sorbents are being developed that do not adversely affect fly ash marketability. Most of the other technologies listed in Table 7 are installed after an ESP or fabric filter, and therefore preserve fly ash sales. They typically act as a polishing device for the particulate matter.

The electron beam-flue gas treatment (EB-FGT), plasma corona discharge (PCD) and dielectric barrier discharge (DBD) technologies are designed to remove SO2 and NOx with ammonia injection, producing a saleable fertiliser by-product. The commercial ECO™ system utilises a DBD reactor, but instead of injecting ammonia ahead of the DBD, the ammonia-free flue gas passes through the DBD to oxidise NO and mercury, and then through an ammonia-based wet scrubber and wet ESP. The main drawback of the plasma technologies is the parasitic power consumption, which can reach over 3% of total plant production capacity. The power consumption is largely determined by the amount of NOx oxidation required and the flue gas flow rate. Therefore, lowering the NOx concentration in the flue gas by the use of low NOx burners, for example, could reduce power consumption. Elemental mercury is also oxidised in the plasma reactors, with the ECO™ system capable of removing over 85% of the oxidised mercury. The fate of mercury in the EB-FGT, PCD and DBD demonstration and/or pilot plants was not investigated. Capital and operating costs for the three plasma systems are lower than a conventional wet FGD + SCR system. The operating costs, though, are reliant on the market price for the fertiliser by-product and ammonia reagent.

Both Lextran and LoTOx™ combine ozone injection with wet scrubbing, whilst Eco Power Solutions’ system (EPS system) incorporates oxidation (using ozone and hydrogen peroxide) with condensation. All three technologies have similar removal efficiencies for SO2 and NOx, remove some mercury (over 90% in the EPS and LoTOx™ systems), and produce saleable by-products. LoTOx™ has been installed at petroleum refineries and Lextran at a large-scale Chinese steel plant (sintering machine). The EPS system has yet to be demonstrated at a full-scale plant, but it does include CO2 capture. CO2 removal can be increased from 30% to over 90% when the CO2 Capture Module is fitted. Capital costs are expected to be lower than conventional separate pollutant collection systems for all three systems, and operating costs may be lower, especially if there is a local market for the by-products. The main drawback of all three technologies is their high auxiliary power consumption, mainly due to the on-site ozone generators. Parasitic power generation can reach 3–7% of total plant output. As with the non-thermal plasma technologies, lowering the amount of NOx in the flue gas before the ozone injection point would reduce power consumption. In some cases, ozone emissions may increase due to ozone slip, although this is not a concern in the EPS system.

The Shell Cansolv® system, which sequentially removes SO2 and CO2 from flue gas, is one of the most efficient SO2 capture technologies around. It is currently being installed on the coal-fired Boundary Dam power plant in Canada, where fertilisers will be produced from the recovered SO2 and the captured high purity CO2 will be used for enhanced oil recovery. A number of heat recovery features can be incorporated to lower the high parasitic power consumption. Moreover, new amine solvents are being developed to further lower the energy penalty and operating costs.

The CEFCO process, currently at the pilot stage, has one of the highest SO2, SO3, NOx, CO2 and
## Table 7 Multi-pollutant control processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Pollutants removed</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet scrubbing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limestone wet scrubbers</td>
<td>Wet scrubbing with limestone slurry. Gypsum by-product</td>
<td>95→99% SO_2, &lt;60% SO_3, &gt;98% HCl + HF, 75–99% oxidised Hg (&gt;50% total Hg), &gt;70% PM</td>
<td>commercial</td>
</tr>
<tr>
<td>Airborne Process™</td>
<td>Dry, regenerable sodium bicarbonate injection combined with wet sodium carbonate scrubbing and oxidant wash. Saleable fertiliser by-product</td>
<td>99.9% SO_2 + SO_3, 99% NOx, 99% Hg</td>
<td>commercial</td>
</tr>
<tr>
<td>NeuStream®-MP</td>
<td>Ozone injection for NO oxidation before dual-alkali flat jet scrubber followed by CO_2 capture. Solvents are regenerated. Saleable by-products</td>
<td>97% SO_2, 98% HCl, &gt;90% NOx, &gt;90% oxidised Hg (≈80% total Hg), &lt;95% PM, 70–90% CO_2</td>
<td>commercial demonstration</td>
</tr>
<tr>
<td>SkyMine®</td>
<td>Scrubbing with NaOH, which is electrochemically produced from brine. Saleable by-products include carbonates and/or bicarbonates, H_2 and Cl_2</td>
<td>&gt;99% SO_2 + NO_2, 90% Hg, 80–90% CO_2</td>
<td>commercial demonstration (on cement plant)</td>
</tr>
<tr>
<td>Semi-dry scrubbing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray dry scrubbers</td>
<td>Scrubbing with lime slurry. May incorporate a Hg sorbent</td>
<td>90–98% SO_2, 95–98% SO_3 + HCl, &gt;95% PM, 0–95% Hg</td>
<td>commercial</td>
</tr>
<tr>
<td>Circulating fluidised bed scrubbers</td>
<td>Scrubbing with dry hydrated lime and water in a circulating fluidised bed. May incorporate a Hg sorbent</td>
<td>&gt;98% SO_2, 99% SO_3, HCl + PM, &gt;95% Hg</td>
<td>commercial</td>
</tr>
<tr>
<td>Dry technologies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReACT™</td>
<td>Activated coke fluid bed absorption with sorbent regeneration. Ammonia injection upstream of absorber. Saleable by-products</td>
<td>99% SO_2 + SO_3, 20–80% NOx, &gt;90% Hg, ~50% PM</td>
<td>commercial</td>
</tr>
<tr>
<td>SNOX™</td>
<td>Regenerable catalytic reduction followed by acid condensation. Saleable by-products</td>
<td>99% SO_2 + SO_3, 99% NOx, &gt;99.9% PM</td>
<td>commercial</td>
</tr>
<tr>
<td>Catalytic ceramic filters</td>
<td>NOx catalyst embedded in ceramic filter. Upstream injection of sorbents for removal of SO_2 and Hg</td>
<td>&gt;95% NOx, &gt;99.8% PM, 80–95% SO_2, SO_3 + HCl, &gt;90% Hg</td>
<td>commercial, but not yet demonstrated on large-scale power plants</td>
</tr>
<tr>
<td>Max-9™</td>
<td>Injection of Hg sorbent and electrostatically stimulated fabric filter</td>
<td>99.99% fine PM, &gt;90% Hg</td>
<td>commercial</td>
</tr>
<tr>
<td>TOXECON II™</td>
<td>TOXECON™ injects mercury before compact pulse jet filter. Hot- or cold-side ESP first removes 99% PM. TOXECON II™ injects mercury sorbent into back portion of cold-side ESP</td>
<td>TOXECON™ &gt;85% fine PM, &gt;90% Hg</td>
<td>commercial</td>
</tr>
</tbody>
</table>
mercury removal efficiencies. It is a net generator of water, and saleable fertilisers and other by-products can be produced. Parasitic power consumption is relatively high, and could be excessive in lignite power plants (at ~23%) for the full four module system.

The CSNOx technology captures SO₂, NOx and CO₂, without the addition of any chemicals or heat energy. It has only been demonstrated on flue gas from diesel engines on board ships.

Multi-pollutant control technologies offer a number of benefits over the series of traditional counterparts that would be needed to eliminate the same number of pollutants. Capital investment is
Conclusions

often lower, as well as operating costs, although many rely on by-product sales to be economically competitive. The footprint is generally smaller than conventional counterparts treating a similar volume of flue gas, making them easier to install in retrofit applications, and they often have a shorter installation time. Some of the systems use modular designs that ensure easy scale-up for larger boilers. Impurities in the flue gas can contaminate the solvent used to scrub CO₂. Thus multi-pollutant technologies with high pollutant (especially SO₂) removal efficiencies, but which do not capture CO₂, could lower CO₂ scrubbing costs, if future regulations require its removal.
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