Low water FGD technologies

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CCC/210 ISBN 978-92-9029-530-3

November 2012

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Abstract

Conventional flue gas desulphurisation (FGD) systems require large supplies of water. Technologies which reduce water usage are becoming more important with the large number of FGD systems being installed in response to ever tightening emission regulations. Reducing water loss is particularly important in arid regions of the world. This report reviews commercial and near commercial low water FGD processes for coal-fired power plants, including dry, semi-dry and multi-pollutant technologies. Wet scrubbers, the most widely deployed FGD technology, account for around 10-15% of the water losses in power plants with water cooling systems. This figure is considerably higher when dry/air cooling systems are employed. The evaporative water losses can be reduced by some 40–50% when the flue gas is cooled before it enters the wet scrubber, a common practice in Europe and Japan. Technologies are under development to capture over 20% of the water in the flue gas exiting the wet scrubber, enabling the power plant to become a water supplier instead of a consumer. The semi-dry spray dry scrubbers and circulating dry scrubbers consume some 60% less water than conventional wet scrubbers. The commercial dry sorbent injection processes have the lowest water consumption, consuming no water, or a minimal amount if the sorbent needs hydrating or the flue gas is humidified to improve performance. Commercial multi-pollutant systems are available that consume no water.

Acronyms and abbreviations

ABS	ammonium bisulphate
AC	activated coke
ACI	activated carbon injection
CapEx	capital expenditure
CCS	carbon capture and storage
CDS	circulating dry scrubber
CFB	circulating fluidised bed
CFD	computational fluid dynamics
DSI	duct sorbent injection
ESI	economiser sorbent injection
ESP	electrostatic precipitator
FGD	flue gas desulphurisation
FSI	furnace sorbent injection
gal	gallon
GSA	gas suspension absorption
ID	induced draft
O&M	operation and maintenance
OpEx	operating expenditure
ppm	parts per million
ppmv	parts per million by volume
PRB	Powder River Basin (USA)
SCR	selective catalytic reduction
SDS	spray dry scrubber
SNCR	selective non-catalytic reduction
SR	stoichiometric ratio
SRS	sulphur reactor system
TMC	transport membrane condenser

Conversion lb/Btu to kg/kJ multiply by 0.4299 (that is, 0.4536/1.055)

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I Introduction

When coal is combusted in a power plant boiler, the sulphur in the fuel combines with oxygen to form sulphur dioxide (SO_2) and small amounts of sulphur trioxide (SO_3) . Further amounts of SO₃ are generated in the selective catalytic reactor, which is widely used for NOx control. Both SO₂ and SO₃ are undesirable for a number of reasons. Sulphur dioxide has been linked with the formation of acid rain, urban smog and health hazards. Sulphur trioxide, if present in sufficient quantity, can form sulphuric acid, leading to corrosion and fouling of power plant equipment and plume opacity problems.

According to the US Environment Protection Agency, power plants are responsible for 66% of worldwide SO₂ emissions, with the majority (over 98%) coming from coal-fired power plants (Morris, 2012). In 2009, coal-fired power plants provided about 40% of the world's electricity. Under the New Policy Scenario of the International Energy Agency's *World energy outlook 2011*, coal demand is expected to continue to grow in the emerging economies for the next 10 y, driven in particular by the power generation industry in China and India (IEA, 2011). Consequently, SOx (SO₂ + SO₃) emissions will increase unless captured. Coal is widely distributed around the world, and is the most abundant fossil fuel with reserves totalling 1 trillion tonnes or some 150 y at current production rates. Hence coal is likely to remain a major fuel source for power generation for some time, although its overall share in the global power generation industry is expected to restrict the rising CO₂ emissions to limit the global temperature increase, then coal demand is likely to decrease earlier. This is unless an effective, and not too expensive system for CO₂ capture and storage is developed.

With the concern over the environmental and health consequences of sulphur oxide (SOx) emissions, various legislation and regulations have been implemented limiting the amount of these and other air pollutants that can be emitted from coal-fired power plants and other industrial facilities. The regional and national emission limit values for SO₂ and other major air pollutants from coal combustion plants are given in the IEA Clean Coal Centre's freely available emissions standards database (*see* www.iea-coal.org.uk/site/2010/emission-standards).

The legislation and regulations have become increasingly stringent over the years, and this continues to be the case today, with new regulations further tightening controls on emissions of air pollutants. An example is the revised Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, which was finalised in May 2012 at a meeting of the Convention on Long-range Transboundary Air Pollution in Geneva. The Protocol sets national emission reduction commitments for the main air pollutants (and includes for the first time PM_{2.5}, particulate matter less than 2.5 µm in diameter) to be achieved by 2020. As part of the agreement, the European Union member states, for example, are jointly committed to reduce their SO₂ emissions by 59% between 2005 and 2020 (UNECE, 2012). The Protocol also sets emission limits for specific emission sources and the required best available technologies to be used to control them. The European Union is revising the Industrial Emissions Directive (IED), which will supercede the current Large Combustion Plant Directive in 2016. This will introduce stricter controls on levels of SO₂ and other air pollutants from industrial facilities over a longer timescale (Hitchin, 2011). China has recently issued a new emission standard for thermal power plants (GB 13223-2011), where SO₂ is now limited to 50 mg/m³ in nine key regions, and to 100 or 200 mg/m³ for new or existing plants, respectively, in the rest of the country. In addition, in several provinces which are dependent on the use of local higher sulphur coals, the SO_2 limits are relaxed to 200 or 400 mg/m³ for new and existing plants, respectively (Minchener, 2012). The standard also, for the first time, limits mercury emissions to 0.03 mg/m³. Several regulations are set to target SOx emissions in the USA, including the proposed Cross State Air Pollution Rule (which replaces and strengthens the 2005 Clean Air Interstate rule) and the secondary National Air Ambient

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Air Quality Standards. While the Mercury and Air Toxics Standards (also known as utility Maximum Achievable Control Technology rules) do not limit SO_2 emissions directly, an alternative is provided wherein power plants can meet a SO_2 standard in place of the hydrogen chloride (HCl) limit. Plants can opt to meet the SO_2 limit instead of installing HCl monitoring equipment (Morris, 2012).

There are various measures for controlling SOx emissions from coal combustion. Flue gas desulphurisation (FGD) is an effective measure that is applied widely on coal-fired power plants. The market for FGD equipment is expected to increase as power plant operators install FGD systems or upgrade their existing systems in order to meet stricter SOx emission levels. Otherwise they will have to shutdown the power plant or switch to a low sulphur fuel, such as natural gas (which requires substantial modifications and may be too costly for older coal-fired power plants). Switching to a low sulphur coal can sometimes bring SOx emissions within acceptable levels, as can cofiring with biomass. New coal-fired power plants will usually need to install an FGD system to comply with emission regulations.

There are a wide range of commercially available FGD processes for removing SOx from flue gas. The processes can be categorised by their water usage, namely wet processes (wet scrubbing), which consume the largest amount of water, followed by the semi-dry and the dry processes. Wet scrubbing is by far the most common FGD system, with a share of over 80% of the total installed worldwide FGD capacity. Semi-dry processes account for less than 10%, and the dry processes for a smaller proportion. In addition, some multi-pollutant systems capture SO₂. Large amounts of water are used in coal-fired power plants, with wet scrubbers commonly the second largest consumer of water in plants with water cooling systems. The biggest use of water is for condenser cooling. Studies have shown that the per capita availability of water is reducing (Couch, 2005). Therefore competition between agricultural, urban/domestic and industrial use is likely to intensify. Moreover, many power plants are built, or are being built, in arid areas or areas subject to drought, including regions in Australia, China, South Africa, and the USA. Consequently, low water FGD processes would be preferred in these situations.

This report discusses low water FGD processes for coal-fired power plants. It covers processes that are or nearly commercial, but not those that are at the early stages of development. The report begins by discussing the fundamentals of FGD. The next chapter examines wet scrubbers, the most common FGD system. Over half the water in the flue gas can be lost in wet scrubbers due to evaporation. Technologies being developed to reduce the evaporative water losses or to recover the flue gas water vapour for recirculation are reviewed. For the purposes of this report, low water FGD systems are defined as those that consume less than 60% of the amount used by conventional wet scrubbers. Semi-dry scrubbing systems, where the water consumption is between the wet and dry processes, are covered in Chapter 4. These include the spray dry scrubbers (lime spray scrubbers) and circulating dry scrubbers. The commercial dry sorbent injection processes are discussed in Chapter 5. They essentially consume no water, or only a minimal amount. Finally, multi-pollutant systems, including those where the desulphurisation component can be installed separately, are described. The economics of the processes are site-specific, and therefore are discussed only in general terms.

2 FGD fundamentals

Sulphur occurs in coal in three main forms, as:

- organically-bound sulphur;
- sulphide minerals (pyritic sulphur);
- sulphate minerals (sulphate sulphur).

During combustion both the organic and pyritic sulphur are oxidised to SO_2 . Some of the SO_2 is further oxidised to SO_3 , catalysed by the presence of transition metals in the coal. Overall, around 0.5% to 2% of fuel sulphur is typically oxidised to SO_3 in the boiler (Moser, 2006), the amount depending on the boiler design, coal sulphur content and combustion conditions. The sulphate minerals represent a small fraction of the total sulphur in coal and have no significant role in the combustion process itself or in contributing to emissions. Small amounts (~5–10%) of the fuel sulphur may be retained in the fly ash and the remainder, in the absence of emissions control, escapes to the atmosphere, principally as SO_2 . On the other hand, some coals, such as the US Powder River Basin (PRB) subbituminous coals, produce virtually no SO_3 . Their highly alkaline fly ash removes the bulk of any SO_3 that is generated (EPRI, 2007).

The combustion of high sulphur coals and cofiring coal with high sulphur fuels, such as petroleum coke or residual fuel oil, can increase the amount of SO₂ and SO₃ in the flue gas. The installation of Selective Catalytic Reduction (SCR) units, widely used for NOx control, leads to catalytic oxidation of SO_2 , which can more than double the amount of SO_3 in the flue gas passing through it. The amount of SO₂ converted to SO₃ is a function of the catalyst properties. Poisoning of SCR catalysts and fouling of downstream equipment, such as air heaters, can occur due to the reaction of SO_3 with ammonia (used in the SCR units). SO₃ combines with moisture in the flue gas to form sulphuric acid. Problems with corrosion can result if the acid condenses on air heater surfaces, in ducts or other equipment (such as electrostatic precipitators (ESPs) or induced draft (ID) fans). Hence it is important to keep the back-end temperatures above the acid dew point. But raising the air heater outlet temperature to avoid corrosion has a negative effect on unit efficiency. When SO_3 or vapour phase sulphuric acid is emitted into the atmosphere and cools, fine particles of sulphuric acid aerosol are formed. The visible plume appears as a blue-white haze or a brown-orange cloud, depending on atmospheric conditions. The effect is more prominent in power plants with wet FGD systems fitted for SO_2 control. The threshold concentration above which a visible plume may be seen is ~5 ppmv in the stack discharge (Gray and others, 2008). Regulations on plume opacity are becoming more stringent in countries such as the USA, and therefore the importance of SO₃ removal. The terms 'SO₃' and 'sulphuric acid' represent different forms of the same pollutant and are often used interchangeably in the literature, as is the case in this report.

 SO_3 in the flue gas can absorb onto the fly ash and activated carbon injected to control mercury emissions, consequently competing with mercury for active adsorption sites. Thus the removal of SO_3 can have a number of benefits by mitigating these problems. For example, removing 90–95% of the SO_3 will reduce the acid dew point of the flue gas by around 4–16°C (depending on the SO_3 level), thereby providing protection against acid corrosion for all equipment and ductwork downstream of the sorbent injection point. This lower acid dew point allows for flexibility in the temperature of operation of the air heater and, in some cases, can result in substantial savings by improving heat rate (Wilhelm, 2004). If the power plant's mercury control strategy includes the use of a high oxidation catalyst in its SCR system for enhanced oxidation of mercury (and its subsequent removal in a wet FGD system), removal of the additional SO_3 generated across the catalyst will be essential to avoid the negative impacts discussed above (Moser, 2007). However, SO_3 is not always undesirable as low concentrations are essential for adequate ESP performance. If there is insufficient levels of SO_3 , then flue gas conditioning may be required. SO_3 issues for coal-fired plants have been reviewed in the IEA Clean Coal Centre report by Fernando (2003). There are a wide range of commercially available FGD processes for removing SO_2 and/or SO_3 from flue gas. They differ in terms of sorbent used, by-products produced, SO_2/SO_3 removal efficiency, and costs. The major processes can be categorised by the amount of water consumed, namely:

- wet processes, which use the highest amount of water;
- semi-dry processes, where water consumption is between the wet and dry processes;
- dry processes which consume no process water, or only a minimal amount.

These processes can be further classified into 'once-through' or 'regenerable', based on how the solids generated by the process are handled. Once-through systems either dispose of the spent sorbent as a waste or utilise it as a by-product. Regenerable systems recycle the sorbent back into the system. Regenerable processes generally have higher costs than once-through processes. However, regenerable processes may be preferred if space or disposal options are limited and markets for by-products are unavailable.

Almost all commercial FGD processes are based on the fact that SO_2 and SO_3 are acidic and so can be removed by reaction with a suitable alkaline sorbent. The most commonly used material is limestone (calcium carbonate) due to its availability and price. Quicklime (calcium oxide) is more reactive than limestone due to its higher surface area and porosity. Hydrated or slaked lime (calcium hydroxide) is more reactive than either limestone or quicklime. Both quicklime and hydrated lime are made by heating limestone (calcination). Compounds, such as fly ash, may be mixed with the calcium-based sorbents to improve their reactivity and performance. Other common sorbents used include sodium-based compounds (sodium carbonate, bicarbonate and trona), magnesium carbonate and ammonia. The sorbents react with SO_2 and SO_3 in the flue gas to produce a mixture of sulphite and sulphate salts. The proportions of sulphite and sulphate are determined by the process conditions; in some processes, all the sulphite is converted to sulphate (DTI, 2000). The sorbents also react with any gaseous sulphuric acid to form sulphate and bisulphate compounds.

In wet FGD processes, the flue gas is brought into contact with the sorbent (either as a solution or more commonly as a slurry) in a separate absorber unit (wet scrubber). The SO_2 in the flue gas dissolves in the water to form a dilute acid solution that then reacts with, and is neutralised by, the dissolved alkaline sorbent. The sulphite and sulphate salts produced precipitate out of solution, depending on the relative solubility of the different salts present. Calcium sulphate, for example, is relatively insoluble and readily precipitates out. Sodium and ammonium sulphates are much more soluble.

In dry and semi-dry systems, the sorbent is brought into contact with the flue gas, either by injecting or spraying it into the gas stream or by passing the flue gas through the sorbent in a separate vessel. In either case, SO_2 and SO_3 react directly with the solid to form the corresponding sulphite and sulphate. For this to be effective, the solid needs to be porous and/or finely divided. In semi-dry systems, water is added to the flue gas to form a liquid film on the particles in which the SOx dissolves, promoting the reaction with the solid (DTI, 2000). In some processes, the sorbent is introduced as a concentrated slurry or solution. The spent sorbent, along with the fly ash (if it is not pre-collected), is removed in the particulate collection device – a cold-side ESP or fabric filter (baghouse).

2.1 Chemistry

The performance of sorbents is a function of a number of variables such as particle size, morphology, temperature, sorbent dispersion, reactivity and residence time. A smaller particle size usually improves SO_2 and SO_3 removal efficiency, and less material is required to achieve the same removal level. If milling on-site, then the cost of doing so must be balanced against the cost of the equipment and maintenance. Particle size is more important for plants with ESPs than fabric filters since there is a longer contact time through the fabric filter cake buildup for reactions to continue.

One measure of the performance of sorbents is its utilisation. This is the efficiency with which the sorbent fed to the FGD system reacts with SO_2 (or SO_3). Sorbent utilisation is generally better with wet FGD processes than with dry and semi-dry ones, and better at low SO_2 removal efficiencies than high ones. It depends on many variables, as listed above, as well as the concentration of SO_2 entering the FGD vessel. Sorbent utilisation is usually expressed in terms of the stoichiometric ratio (SR). SR is defined as moles of reagent per mole of SO_2 . Different methods for calculating the SR are applied for wet and dry/semi-dry processes. In wet FGD processes, the SR is calculated as moles of reagent per mole of SO_2 removed, whereas dry/semi-dry processes calculate the SR as moles of reagent per mole of SO_2 at the inlet to the FGD system (Sargent and Lundy, 2007). Thus care is required when comparing SR values for wet and dry/semi-dry processes.

The following sections outline the principal reactions occurring between calcium- and sodium-based sorbents and SO_2 and SO_3 as these are the more commonly used sorbents in dry and semi-dry processes. Calcium-based sorbents (limestone) is the most common sorbent used in wet scrubbers.

2.1.1 Calcium-based sorbents

The reactions of limestone (CaCO₃) and hydrated lime (Ca(OH)₂) with SO₂ and SO₃ are influenced by the temperature. In the power plant furnace (*see* Section 5.1), at optimum temperatures between 980 and 1230°C, calcination of the limestone and dehydration of the hydrated lime occur to form quicklime (CaO):

$$CaCO_3 \rightarrow CaO + CO_2$$

 $Ca(OH)_2 \rightarrow CaO + H_2O$

The calcium oxide then reacts with SO_2/SO_3 and oxygen in the flue gas to produce calcium sulphate (CaSO₄):

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$$
$$CaO + SO_3 \rightarrow CaSO_4$$

Spray dry scrubbers (*see* Section 4.1) and the duct spray process (*see* Section 4.2) inject the calcium hydroxide sorbent as a slurry. The heat in the flue gas evaporates the water from the slurry and, at the same time, the evaporation cools the flue gas. The calcium hydroxide then reacts directly with SO₂ to form calcium sulphite hemihydrate (CaSO₃.¹/₂H₂O), as the temperature is too low for its dehydration:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O + \frac{1}{2}H_2O$$

A smaller portion of the SO_2 can also react with oxygen in the flue gas and the calcium hydroxide to produce calcium sulphate dihydrate (gypsum):

$$Ca(OH)_2 + SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow CaSO_4.2H_2O$$

In addition, the SO₃ reacts with calcium hydroxide (EPRI, 2007) as follows:

$$Ca(OH)_2 + SO_3 + H_2O \rightarrow CaSO_4.2H_2O$$

Circulating dry scrubbers (*see* Section 4.3) typically utilise dry calcium hydroxide and inject water separately into the flue gas to improve the SO_2 removal efficiency. The chemical reactions of the sorbent with SO_2 and SO_3 are similar to those given above for spray dry scrubbers. Some dry sorbent injection processes (*see* Chapter 5) also inject dry calcium hydroxide which reacts similarly with SO_2

and SO3 to produce calcium sulphite and sulphate, respectively.

The principal reactions occurring in the limestone wet scrubbers with forced oxidation (*see* Section 3.1) are:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + H_2O + CO_2$$
$$CaSO_3 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4.2H_2O$$

In the absence of oxygen, the calcium sulphite precipitates out as a hemihydrate (CaSO₃. $\frac{1}{2}$ H₂O), which is difficult to handle. Hence oxygen is injected into the reaction tank at the bottom of the absorber to oxidise the calcium sulphite to gypsum, as shown in the last equation above (European Commission, 2006).

2.1.2 Sodium-based sorbents

Solid sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃) and trona are the dominant sodium-based sorbents used for FGD. Trona (Na₂CO₃.NaHCO₃.2H₂O) is a naturally occurring sodium sesquicarbonate mineral, produced as a fine powder.

Sodium bicarbonate and trona thermally decompose to form sodium carbonate when injected into hot flue gas (above ~125°C):

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$
$$2(Na_2CO_3 NaHCO_3 2H_2O) \rightarrow 3Na_2CO_3 + CO_2 + 5H_2O$$

The evolution of water vapour and carbon dioxide creates a network of void spaces (micropores) throughout the particles, a phenomenon often called the 'popcorn' effect. It results in a much higher surface area, around 5 to 20 times the original surface area, depending on the sorbent (European Commission, 2006). The specific surface area for trona is ~10 m²/g (Kong and Wood, 2010). This relatively high surface area enables fast reactions between sodium carbonate and SOx. The generated or natural sodium carbonate reacts with SO₂ or SO₃ to produce sodium sulphite (Na₂SO₃) or sodium sulphate (Na₂SO₄) as follows:

$$Na_{2}CO_{3} + SO_{2} \rightarrow Na_{2}SO_{3} + CO_{2}$$
$$Na_{2}CO_{3} + SO_{2} + \frac{1}{2}O_{2} \rightarrow Na_{2}SO_{4} + CO_{2}$$
$$Na_{2}CO_{3} + SO_{3} \rightarrow Na_{2}SO_{4} + CO_{2}$$

Because of the 'popcorn' effect, sodium bicarbonate is more efficient in removing SO_2/SO_3 than trona, which in turn is more efficient than purchased sodium carbonate. Cho (2007) has developed a method for converting the Na₂CO₃ fraction of the parent trona to NaHCO₃ to improve SOx removal efficiency in dry sorbent injection systems. A 20% increase in SO₂ removal was achieved with the modified trona at a SR ratio of 1. However, trona is more difficult to handle than hydrated lime or other typical powdered sorbents due to the small particle size (~28 µm average particle size) and cohesiveness of the product. It has a chemical affinity to water and therefore needs to be very dry (<0.04% free moisture) to avoid handling problems, such as flow blockages due to agglomeration (Ritzenthaler, 2007; Ritzenthaler and others, 2007). Sodium bisulphite (NaHSO₃) and sodium sulphite (Na₂SO₃) are injected as solutions to remove SO₃ (*see* Section 5.3.2) according to the following chemical reactions:

$$NaHSO_3 + SO_3 \rightarrow NaHSO_4 + SO_2$$
$$Na_2SO_3 + 2SO_3 + H_2O \rightarrow 2NaHSO_4 + SO_2$$

When the Na:SO₃ molar ratio exceeds 1, then the reactions (Wilhelm, 2004) become:

 $2NaHSO_3 + SO_3 \rightarrow Na_2SO_4 + 2SO_2 + H_2O$ $Na_2SO_3 + SO_3 \rightarrow Na_2SO_4 + SO_2$

2.2 CO₂ emissions

The type of FGD technology installed influences overall CO_2 emissions from the power plant. All FGD processes require varying amounts of electric power to operate. This adds to the overall parasitic load of the unit, and hence CO_2 emissions. Parasitic power consumption for wet limestone scrubbers is typically between 1–2% of the gross output of the facility. FGD processes that utilise a carbonate-based reagent (such as limestone, sodium carbonate, sodium bicarbonate and trona), form CO_2 as a by-product of the chemical reactions of the reagent with SO_2 (*see* Section 2.1). For a typical unit, CO_2 emissions from the wet limestone scrubber can add an extra 1% to the overall CO_2 emissions, but it can be as high as 3% for facilities burning high sulphur coals.

Although by-product CO_2 is not generated by the lime-based processes, CO_2 is produced during the manufacture of lime. Limestone is heated in the absence of oxygen to remove a molecule of CO_2 , as shown in the following equation:

$$CaCO_3 + heat \rightarrow CaO + CO_2$$

Unless the CO_2 from the on-site lime kiln is captured and stored, overall CO_2 emissions from plants with lime-based scrubbers (dry scrubbers) will be similar to those using wet scrubbers (US EPA, 2010).

 CO_2 capture and storage from coal-fired power plants is of increasing concern. There are several commercially available technologies which could be used for capturing CO_2 from flue gases. Absorption processes based on chemical solvents are currently the preferred option. They offer high capture efficiency and selectivity, and the lowest energy use and costs when compared with other existing post-combustion capture processes. The presence of SOx, water vapour and other impurities in the flue gas affects CO_2 removal. The allowable SOx content is determined primarily by the cost of the solvent, since the solvent is consumed by reaction with SOx. Amines, such as monoethanolamine, may require SOx concentrations of around 10 ppm (~20 mg/m³) to keep the solvent consumption and makeup costs at reasonable values (Adams, 2010). An additional FGD step may be necessary if the FGD system cannot meet the required SOx level. The effects of flue gas impurities on post-combustion CO_2 capture technologies are discussed in the IEA Clean Coal Centre report by Adams (2010).

2.3 By-product utilisation

The solid products from dry and semi-dry FGD processes are mostly or completely dry and are therefore easily handled, unlike those from wet FGD processes. The limestone wet scrubbers commonly produce gypsum, a saleable product. Applications for gypsum include wallboard

manufacture, the cement and concrete industry, gypsum-based plasters and mortars, and agriculture as a soil amendment. The market for gypsum (and any saleable by-product from the various FGD processes) is largely 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 would be unable to sell all of their by-products. A market for the products from the dry and semi-dry processes needs to be developed otherwise this could become a barrier for further implementation of the technologies.

A concern with dry and semi-dry processes is the effect of the spent sorbent on the saleability of the fly ash. If the fly ash cannot be sold, then it is landfilled at a cost to the plant operator. One of the main markets for fly ash is in the production of cement and concrete products. In the semi-dry processes (dry scrubbers - see Chapter 4), the pre-collection of fly ash is widely practised in Europe but is not as common in the USA. Ash from the circulating fluidised bed scrubbers is usually pre-collected in China (Jiang and others, 2011). Pre-collecting the fly ash allows it to be sold, generating income for the plant operator. In general, the by-products from the different processes, which typically use a calcium hydroxide sorbent, have similar chemical, physical and mineralogical properties. The properties vary from unit to unit as the quantities and characteristics of the by-products are affected by factors such as the coal type and composition, combustion conditions, sorbent composition, SO₂ uptake efficiency (Ca:S ratio), fly ash collection location and efficiency, composition and mineralogy of the fly ash, sorbent recirculation rate, and load level (Heebink and others, 2007). The by-products consist principally of calcium sulphite, calcium sulphate, calcium hydroxide and calcium carbonate. Commercial applications include road construction, landscaping, mine backfilling, acid mine drainage control, light weight aggregates, fertilisers, and reagent in wet FGD processes. The latter two require a low fly ash concentration. These and potential applications have been reviewed by the University of North Dakota Energy & Environmental Research Center (2007).

In the sorbent injection processes, where the sorbent is injected into the ductwork, the solid products are collected with the fly ash in the particulate collection device. Fly ash that contains too high a level of sodium cannot be used by the cement industry. Consequently, the recovered fly ash/spent sorbent mixture from sodium-based processes (*see* Section 5.3) typically has little economic value. The sodium sulphate and, to a lesser extent, sodium sulphite reaction products are water soluble and so could leach into soils and the water table when landfilled. Therefore their disposal can be expensive. Collecting the fly ash before the sorbent injection point could allow the fly ash to be sold.

Ammonia (*see* Section 5.3.2) tends to be adsorbed readily on the fly ash from high sulphur coals, and could substantially modify the range of potential commercial uses for the ash. The solid reaction products, ammonium sulphate and ammonium bisulphite, are readily soluble in water, liberating ammonia into the air with just the moisture from the air. This can result in a strong odour of ammonia even at very low concentrations of ammonia in the fly ash. Fly ash with high amounts of ammonia will be unacceptable for use in concrete due to the odour problems associated with the mixing, pouring and curing of concrete. However, additives or other beneficiation processes are available to solve this problem (EPRI, 2007). If the ammonium sulphate is collected separately from the fly ash than it could be sold as a fertiliser product.

Applications for the by-products from sorbent injection processes are being investigated. Potential applications of the fly ash/spent sorbent mixtures, when using calcium-based sorbents, include road construction, landscaping, and mine backfilling. If the calcium sulphate is collected separately from the fly ash then it could be sold as a fertiliser. More research on ways to utilise the spent sorbent mixture from dry and semi-dry processes is needed.

3 Wet scrubbers

Large amounts of water are consumed within a coal-fired power plant for cooling purposes, FGD make-up, boiler make-up and other uses. The amount consumed varies depending on the type of plant (subcritical, supercritical or ultra-supercritical), the cooling system employed, the FGD process and many other factors.

Make-up water usage within a subcritical and a supercritical 550 MW coal-fired power plant is illustrated in Figure 1. The plants utilise a wet scrubber (limestone forced oxidation process) for FGD and a wet cooling tower (the most common type of cooling system). The figure shows that the cooling system is the largest water consumer, followed by the FGD and boiler units. The total make-up water usage without carbon capture and storage (CCS) was calculated to reach 2654 L (701 gal)/MWh for the subcritical plant and 2411 L (637 gal)/MWh for the supercritical case (Zhai and others, 2009). The lower steam cycle heat rate of a supercritical plant compared to a subcritical one means that less heat needs to be rejected from the condenser. Hence lower amounts of cooling water, and therefore make-up water, are required.

The changes in make-up water usage with the inclusion of CO_2 capture (using an amine-based system) are also shown in Figure 1. The increased steam cycle heat rate and additional electricity requirements for CO_2 capture result in more steam, and higher SO_2 and CO_2 emissions, which in turn lead to a significant increase in make-up water usage for the boiler, FGD, and cooling systems. Make-up water usage of the boiler and the FGD increases by around 45 to 50% for both subcritical and supercritical plants, whereas the make-up water in the cooling systems increases by ~90% for both cases. The total make-up water is 4944 L (1306 gal)/MWh for the subcritical case and 4387 L (1159 gal)/MWh for the supercritical plant, an overall increase of over 80% in both cases. The make-up water required for the FGD system in the supercritical plant without CCS is 6% less then the subcritical case and 9% lower with CCS. This is because SO_2 emissions are lower for supercritical plants.



Figure 1 Make-up water usage in subcritical and supercritical plants (Zhai and others, 2009)

Table 1 Water consumption and losses in power plants (data from Klett and others, 2007)								
	Subcritical power plant		Supercritical power plant					
	L/min (gal/min)	L/MWh (gal/MWh)	L/min (gas/min)	L/MWh (gal/min)				
Raw water consumption	21,800 (5759)	2514 (664)	19,400 (5125)	2249 (594)				
Water to FGD system	2162 (571.1)	249 (65.8)	1899 (501.6)	220 (58.1)				
Make-up water to cooling tower	19,495 (5150)	2247 (593.6)	17,371 (4589)	2013 (531.8)				
Make-up water to condenser	145 (38.2)	17 (4.4)	128 (33.9)	15 (3.9)				
Water losses								
Water with gypsum	307 (81)	35.2 (9.3)	269 (71)	31.4 (8.3)				
Boiler flue gas	3,513 (928)	405 (107)	3096 (818)	360 (95)				
Cooling tower blowdown	4,910 (1297)	566 (149.5)	4372 (1155)	506.5 (133.8)				
Cooling tower evaporation	14,729 (3891)	1697.8 (448.5)	13,128 (3468)	1521.4 (401.9)				
Total water losses	23,459 (6197)	2704 (714.3)	20,865 (5512)	2419.3 (639)				

Water consumption and losses for both subcritical and supercritical 500 MW coal-fired power plants were evaluated by NETL in 2005 (Klett and others, 2005) and revised by the authors in 2007 (Klett and others, 2007). Both plants are equipped with limestone forced oxidation FGD systems, utilising a limestone slurry containing 70% water. Here, the cooling water system (wet tower) accounts for nearly 84% of the water loss in both subcritical and supercritical plants (*see* Table 1), with the water loss in the flue gas and FGD system accounting for 16% of the total. If the water lost with the gypsum is excluded, then 15% of the water is lost through the flue gas in both plants. Over half the water that ends up in the flue gas is evaporated from just the FGD system. Water must be added to the system to make up for these evaporative water losses, the amount added being a function of the unit size (flue gas flow) and sulphur feed rate. Wet scrubbers consume some 2160 L/min (571 gal/min) of make-up water in a 500 MW subcritical plant and around 1900 L/min (502 gal/min) in a 500 MW supercritical plant when burning 3 wt% S, dry basis, bituminous coal. The values differ from those in Figure 1 since different assumptions are used in the models.

On a site which utilises dry/air cooling for the condenser, or where it is seawater cooled (once-through cooling system), the use of water in wet FGD systems can easily be 40–70% of the total site usage (Couch, 2005). Only ~10% is used for boiler make-up water. This is because water withdrawal from a local water body (such as a river, lake or the sea) and water consumption for the dry/air cooling system is minimal. Power plants equipped with once-through cooling systems have relatively high water use but low water consumption as the cooling water is returned back to the local water source from which it was withdrawn. Wet cooling towers have relatively low water use but high water consumption compared with once-through systems since only make-up water (to replace evaporative water losses and blowdown) is withdrawn. The cooling water is recycled in the system. Power plants with a hybrid cooling system (which uses both air and water for cooling) will have a water consumption between those with a wet cooling tower or an air/dry cooling system.

This chapter begins by describing limestone wet scrubbers before looking at methods designed to lower their water consumption, namely the reduction of evaporative water losses and recovering water vapour from the flue gas. The treatment of scrubber waste water to enable it to be recycled to the FGD system, thus lowering fresh water consumption, is outside the scope of the report.

3.1 Limestone wet scrubbers

The limestone FGD process is the most widely deployed technology for removing SO₂ from flue gas. 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. As noted above, limestone wet scrubbers consume some 2160 L/min of make-up water in a 500 MW coal-fired subcritical plant (about 4.32 L/min per MW or 1.14 gal/min per MW) and around 1900 L/min in a 500 MW supercritical plant (about 3.8 L/min per MW or 1 gal/min per MW) when burning bituminous coal (Klett and others, 2007). These figures, though, are dependent on a number of factors. Typical water consumption figures quoted by Adamson (2008) are 5.7–6.8 L/min per MW (1.5–1.8 gal/min per MW). Wet scrubbers commonly remove 95–98% of the SO₂, with the latest generation capable of removing 99%. They also remove hydrogen chloride (HCl), hydrogen fluoride (HF), and oxidised mercury (but not elemental mercury), and have been installed on units burning low to high sulphur coals.

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. The absorber unit is usually installed downstream of the particulate control device. In the USA, the flue gas enters the absorber at a temperature of around 120–180°C (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 80-90°C. Passing through the scrubber, with all the evaporation taking place, it is further cooled to ~50°C. The flue gas is then reheated in the heat exchanger (exchanging with the incoming gas) to ~90°C before being emitted (Couch, 2005).

A common type of absorber is the counter-flow open spray tower (*see* Figure 2) 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 SO_2 from the flue gas, facilitating reaction with the limestone. HCl



Figure 2 Limestone wet scrubber system (Otter Tail Power, 2009)

present in the flue gas is also absorbed and reacts with the limestone to form calcium chloride. Some of the water in the spray droplets evaporates, cooling the gas and saturating it with water. The desulphurised flue gas passes through the mist eliminators to remove 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 this slurry to the gypsum processing system. The gypsum is dewatered and processed to produce saleable quality product or is sent for landfill disposal. Water removed from the gypsum is returned to the process. A bleed stream is removed to control the chemistry of the scrubber liquor in the absorber, and this wastewater has virtually no reuse potential within the power plant (Preston and others, 2011). It contains chlorides, heavy metals (including mercury) and other impurities and is treated in the water treatment plant before it is discharged.

Limestone wet scrubbers have been in operation for over 30 y and, with their widespread application, is a well understood technology. They have a high SO₂ removal efficiency (>98%), but do not capture significant amounts of SO₃. If air pollution regulations require SO₃ removal then it could be captured by injecting an appropriate sorbent into the ductwork upstream of the wet scrubber (*see* Section 5.3.2) or, in the form of sulphuric acid, with a wet ESP located after the wet scrubber. Unfortunately, CO₂ is produced as a result of the reaction of limestone with SO₂ (*see* Section 2.1.1) and is emitted with the scrubbed flue gas, thus adding to CO₂ emissions from 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. Otherwise the flue gas can be reheated to above its dew point to minimise corrosion. The absorbers are also handling large volumes of abrasive slurries.

Parasitic power consumption is around 1.2-1.5% when burning low sulphur coals and 1.5-2% with high sulphur coals (Adamson, 2008). This is 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. The gypsum dewatering equipment and wastewater treatment plant is relatively complex and expensive. The wastewater contains impurities originating from the coal, limestone and make-up water, chloride salts and other FGD reaction products. If additives, such as dibasic acid, are introduced to the limestone slurry to improve SO_2 removal efficiency, then these could contaminate the gypsum and wastewater. Several stages are required to treat the wastewater 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 FGD wastewater is typically combined with other water discharges from the plant, such as that from the bottom ash handling system and cooling water, before it is treated. Capital and operating costs are relatively high due to some of the factors discussed above. However, operating costs are often lower than the semi-dry scrubber processes (*see* Chapter 4) at the same SO_2 removal level. The process produces gypsum which can be sold to offset costs.

3.2 Reducing evaporative water losses

Cooling the flue gas from a typical ~140°C to 90–100°C prior to its entry to the wet scrubber reduces the scrubber's evaporative water losses. This can lower the water consumption in wet FGD systems by ~40–50%. The flue gas exits the scrubber at a temperature of ~50°C and is then reheated in plants where the cooling tower is used as the flue gas stack. This improves stack gas dispersion and helps

avoid condensation. Typically, the flue gas cooling system is incorporated with the flue gas reheating system to form a regenerative heat recovery system. Otherwise, the extracted heat could be recovered within the steam cycle, leading to an improvement in plant efficiency. The regenerative heat exchanger is installed either before or after the particulate control device, which is upstream of the wet scrubber. Heat exchangers for flue gas cooling are utilised in coal-fired power plants mainly in Japan and Europe.

As well as lowering the FGD water consumption, there are several other benefits from cooling the flue gas upstream of the wet scrubber (Nakayama and others, 2006; Rencher, 2008), including:

- reduced gas volumes resulting in a smaller FGD system and stack requirements for new plants. For retrofits, the reduced flue gas volume helps to offset the pressure drop associated with the heat exchanger;
- improved performance of ESPs and fabric filters due to reduced gas volume. Existing ESPs benefit from a larger specific collection area and improved fly ash resistivity (resistivity decreases when the flue gas is cooled). The greatest gain is likely to be from low sulphur coals which typically have higher resistivity ash. Fabric filters benefit from a decrease in the air-to-cloth ratio. These benefits translate into smaller particulate control devices for new plants;
- control of SO₃ (sulphuric acid) emissions through condensation on the fly ash (when the heat exchanger is installed upstream of the hot-side particulate collector). SO₃ emissions at the FGD outlet were <0.1 ppm at Japanese power plants;
- improved mercury capture.

Disadvantages (Green, 2007) associated with regenerative heat exchangers include:

- leakage of the unscrubbed gas into the scrubbed gas stream because the unscrubbed gas stream is at a significantly higher pressure than the scrubbed gas stream. A 2% leakage rate has the impact of reducing the wet scrubber SO₂ removal rate from 98% to 96%. Non-leakage heat exchangers have been developed and are commercially available;
- increased power consumption due to the pressure drop across the heat exchanger;
- a corrosive environment due to sulphuric acid condensation. The use of corrosion resistant materials will increase the cost of the heat exchanger. However, acid corrosion can be prevented by controlling the ratio of the particulate concentration to the sulphuric acid concentration. If a high enough concentration of particulates is present, then the sulphuric acid condenses onto the particulates before it is condensed onto the surface of the heat exchanger (Nakayama and others, 2006). Japanese power plants had no problems when the MHI heat exchanger was installed upstream of the hot-side ESP;
- fouling of the heat exchangers could potentially occur as the unscrubbed flue gas is cooled, increasing maintenance costs.

In addition, regenerative heat exchangers are expensive, and can have high operating and maintenance costs.

3.3 Recovery of water vapour

A typical 400 MW coal-fired power plant equipped with a wet FGD unit requires about 30 m³/h (500 L/min) of demineralised make-up water for steam production, whilst emitting 150 m³/h (2500 L/min or 150 t/h) of water vapour through the stack (Daal, 2011; de Vos and others, 2008). Recovering 20% of the emitted water would enable a plant to become self-sufficient, but if over 20% is captured, then the plant would become a water supplier instead of a consumer. Flue gas contains 8–11% of the water vapour in a power plant stack (Daal, 2011), although higher figures are quoted in the literature. Thus capturing flue gas vapour could substantially lower the power plant's water consumption. The captured water could be used as FGD make-up water, transported to the condenser, where it is added to the water steam cycle as additional water to compensate for the steam/water losses, or used elsewhere in the plant.

The moisture in boiler flue gas comes from three sources, namely fuel moisture, water vapour formed from the oxidation of fuel hydrogen, and water vapour carried into the boiler with the combustion air (Levy and others, 2011). Thus the amount of water vapour in flue gas is influenced by the coal type. Subbituminous coal, lignite and brown coal have a higher moisture content than higher rank coals and so contribute more moisture to the flue gas. Depending on the moisture and sulphur contents of the coal, and the technology employed, then the water recovered could provide all the site water for a wet scrubber, for boiler water make-up and for other site uses. Water recovery offers not only the possibility of zero water demand, but also zero liquid discharge.

There are three main ways of recovering water from flue gas:

- condensing it out by cooling;
- filter it out using a membrane; or
- use a desiccant.

3.3.1 Condensing heat exchangers

Researchers at Lehigh University in the USA have conducted laboratory- and pilot-scale tests on the use of condensing heat exchangers to recover water and heat from flue gas. One heat exchanger could be located between the ESP and FGD unit to capture the sensible heat, and additional heat exchangers could be placed between the FGD unit and stack in order to both cool the flue gas (sensible heat transfer) and condense water vapour from the flue gas (latent heat transfer). The captured water can be utilised for power plant cooling or FGD make-up water, whilst the recovered heat could be used in the boiler or turbine cycle to improve boiler efficiency (Levy and others, 2008, 2011).

The pilot-scale tests involved extracting a slip stream after the wet scrubber in a high sulphur bituminous coal-fired power plant and passing it through four heat exchangers in turn. The heat exchangers operated in counterflow with cooling water passing through the tubes and the flue gas flowing outside the tubes. The available cooling water flow rate and temperature governs whether the heat exchangers are better suited for improving unit heat rate or recovering water vapour from flue gas. In the latter case, a likely source of cooling water is the cold boiler feedwater leaving the steam turbine condenser. The flow rate of this feedwater is typically about one half of the flue gas flow rate of the unit and, depending on the time of year and whether the unit uses once-through cooling or a wet cooling tower, the feedwater temperature ranges from about 30°C to 43°C. The colder the cooling water, the greater the water condensation efficiency and the higher the rate of heat transfer. Both these parameters also increase when the cooling water to flue gas flow rate increases. Water vapour capture efficiencies are limited to $\sim 20\%$ when cold boiler feedwater is the cooling fluid. With a cooling water to flue gas flow rate ratio of 2, the condensation efficiency increased from 44 to 71% as the inlet cooling water temperature decreased from 38°C to 24°C. Recovery of water vapour from flue gas could be enhanced through a combination of water- and air-cooled heat exchangers (Levy and others, 2011).

Condensation efficiency is also influenced by coal type, which affects the initial moisture content of the flue gas, and the flue gas temperature. Figure 3 shows that water recovery from flue gas is more efficient with high moisture coals, and at lower flue gas temperatures. Thus high moisture coals are prime candidates for water recovery from the flue gas. For low moisture coals, water recovery by condensation may not be a practical option (Sarunac, 2010).

Condensing flue gas to recover water requires a large cooling capacity, can lead to corrosion and fouling of the heat exchanger, and causes a pressure drop, which is compensated with an ID fan. The presence of sulphuric, hydrochloric and nitric acids (from the flue gas) in the condensate water could potentially corrode the heat exchanger tubes. Inserting an acid trap before the first heat exchanger removed 33% of the dissolved sulphate in its condensate water and 62–76% of the total sulphuric acid captured in the heat exchanger system in the pilot plant tests (Levy and others, 2011). Relatively low



Figure 3 Condensing efficiency as a function of flue gas temperature and coal type (Sarunac, 2010)

cost corrosion resistant 304 SS alloy (or other corrosion resistant materials) could therefore be used for the heat exchanger tubes. Flue gas also contains fine gypsum (CaSO₄) particles which could potentially foul the heat exchanger tubes. The highest calcium concentration was in the condensate water from the first heat exchanger. Utilising an acid trap before the heat exchanger removed 60% of the calcium. However, the recovered water has to be treated before it can be recycled, and this can be costly.

A cost benefit analysis of a 600 MW power plant with one heat exchanger installed downstream of the FGD unit that captures 18% of the flue gas water vapour indicated that it would be cost effective. The capital cost of the heat exchanger is US\$4.14 million, and its annual fixed and O&M costs would be US\$641,019. The latter figure includes the costs for the ID fan and feedwater pump. The capital and annual costs for the ion exchange system, needed to treat the condensate water to enable it to be used in the power generation (18,974 MWh/y) and water savings is US\$1.304 million versus total annual costs of US\$0.703 million (Levy and others, 2011). No dollar value was included for the reduced emissions of mercury and sulphuric, hydrochloric and nitric acids captured in the condensate water. The availability of low temperature flue gas with reduced acid and water vapour content would also lower the cost of capturing CO_2 in amine and ammonia scrubbers.

3.3.2 Membranes

Researchers at the University of Twente, Netherlands, have developed a polymer-based composite hollow fibre membrane that is highly selective for water vapour at flue gas temperatures (Daal, 2011; de Vos and others, 2008). To start the process a vacuum is created inside the hollow fibre, causing a pressure difference. A natural diffusion mechanism then begins, in order to re-establish the equal distribution of the gas molecules inside and outside the tubes. Only the water molecules can pass through the membranes, collecting on the inside of the tubes. The recovered water is of high quality and mineral-free. It can be transported directly to the existing condenser system by applying a

vacuum, where it is added to the water steam cycle as additional water to compensate for the steam/water losses. Any non-condensables are expelled by the vacuum system. No waste water is produced. The pressure drop that occurs over the membrane unit is compensated with an ID fan. The major energy input is electricity to run the vacuum pumps. The net electric efficiency can decrease by 0.1-1.1 percentage points, depending on the heat exchanger lay-out and power plant characteristics (Daal and others, 2012). Combining the water capture membranes with CO₂-selective membranes could lower CO₂ emissions at the same time. The membranes modules are ideally placed after the FGD unit where the flue gas is saturated with water.

Tests in a coal-fired power plant and other industrial plants in the Netherlands and Germany have indicated that at least 40% of the water in the flue gas can be recovered, turning the power plant from a water consumer into a water producer. The recovered water has a high enough quality that it can be employed not only for demineralised water use in the power plant and by industry, but also for public consumption purposes.

An average cost for water from a conventional demineralisation plant in the Netherlands is around $2 \notin m^3$, and would be even higher in dry areas. An economic analysis of the membrane system, based on a membrane lifetime of 3 y and a water flux of 2 L/m²/h, quotes a cost of 1.24–1.38 $\notin m^3$ for the recovered demineralised water, dependent on the configuration of the power plant (de Vos and others, 2008). The price is based on existing power plants and so the price could be lower for new plants. In addition, further savings are possible since the calculations did not include the savings when flue gas reheating is rendered obsolete. Reheating the flue gas to avoid condensation in the stack could be omitted if enough water is removed from the flue gas. Calculations show that a coal-fired power plant can increase its efficiency by about 1%, if reheating is no longer necessary (Daal, 2011). Energy requirements and savings when using membrane technology are further discussed by Daal and others (2012).

The technology is being further developed under the European Union commissioned CapWa (capture



Figure 4 Two-stage TMC integration with a power plant (NETL, 2009)

of evaporated water with novel membranes) project under the leadership of Kema in the Netherlands. Participants include companies from Europe, the Middle East and Africa, including those operating in arid areas. The aim is to develop a water capture module ready for industrial use in 2013-14. The membrane modules will be demonstrated at the Ruthenberg coal-fired power plant in Israel, a gas-fired power plant in Spain, and industrial plants elsewhere (Daal, 2011). More information about this project can be found on the website <u>www.watercapture.eu</u>.

The Gas Technology Institute in the USA is also developing a membrane system to recover up to 90% of the water vapour from flue gas. It is based on their commercial, patented Transport Membrane Condenser (TMC) technology (a nanoporous ceramic membrane) that was originally developed for industrial gas-fired boilers. Again, the recovered water is mineral-free and so can be used directly for boiler and/or FGD make-up water, and/or other uses, depending on the amount of water recovered. A two stage TMC system is being developed for coal-fired power plants that uses two separate cooling water streams to maximise recovery of both the water and latent heat in the flue gas (*see* Figure 4). The inlet water for the first stage TMC unit is obtained from condensate from the steam turbine condenser, whilst the second stage TMC unit, with recovered water vapour and associated latent heat from the flue gas, passes to the deaerator for boiler water make-up. The second TMC unit's outlet water and recovered flue gas water is returned to the cooling water stream. The TMC unit is placed between the FGD unit and stack (NETL, 2009; Wang, 2008; Wang and others, 2012). The system has been tested on a slipstream from a coal-fired power plant in Baltimore, MD, USA.

3.3.3 Liquid desiccants

A liquid desiccant-based dehydration process has been developed, and tested at pilot-scale, by the University of North Dakota's Energy and Environmental Research Center in the USA that recovers 50–70% of the water in the flue gas from a wet scrubber (Feeley and others, 2006; Folkedahl and others, 2006). The technology is already used on a large scale for dehydration of air (air conditioning systems) and natural gas conditioning.

The process involves cooling the flue gas before passing it through an absorption tower in which the liquid desiccant (such as calcium chloride, lithium bromide or triethylene glycol) is injected through up to six spray levels. A packed bed configuration was also tested. The flue gas lean in water exits the absorber, and is passed through a mist eliminator to remove any entrained desiccant droplets before it is discharged through the stack. The water-loaded desiccant is heated via a heat exchanger before entering the regenerator, as the hotter the desiccant the easier it is to separate the water. The water vapour is separated from the desiccant solution in a flash drum by differential pressure, and is recovered in a downstream condenser. The regenerated hot desiccant solution is filtered to remove insoluble contaminants, and is then cooled via a heat exchanger, before it is injected back into the absorber. The colder the desiccant solution, the more water it can pick up. In subbituminous coal tests, and with a desiccant flow of 151–416 L/min (40–110 gal/min), about 0.3–0.9 L/min (0.08–0.23 gal/min) of water was recovered (Carney and others, 2008).

Low grade heating and cooling sources available in a power plant could be utilised to minimise the power needs of the process. Depending on the amount of water to be removed from the flue gas, the system can be designed with no parasitic power consumption, other than pumping loads, by taking advantage of the heat of absorption and the heat of vaporisation to provide the necessary temperature changes in the desiccant between the absorber and the regeneration tank (Folkedahl and others, 2006). Pilot-scale tests indicated that the presence of sulphur in the flue gas was not detrimental and that the process could actually lead to a further reduction in sulphur emissions (Copen and others, 2005). SO₂ capture is primarily influenced by the desiccant pH. The recovered water has a similar quality to that from reverse osmosis treatment, which is normally used to produce boiler make-up water. It can be used for various plant needs as recovered or as direct cycle make-up after minimal treatment.

An economic analysis by Folkedahl and others (2006) for a 250 MWe coal-fired power plant treating a flue gas slipstream in the desiccant system (capacity 284 L/min (75 gal/min)) put the investment costs (equipment and installation) at US\$5,837,762. Auxiliary power consumption would be ~1,051 kW. The total annual operating costs were estimated to be US\$503,860. About 123 million litres (32.4 million gallons) of water would be produced per year, resulting in a price of 0.0053 US\$/L (0.02 US\$/gal or ~4.4 US\$/m³) of pure water. Whether this is economically viable depends very much on the location of the plant. The calculations were carried out for a power plant located in Wyoming, USA.

Questions remain as to the long-term interaction of the desiccant with the flue gas, contamination of the desiccant solution by flue gas constituents, and precipitates that may form and how to handle them. Corrosion could be an issue with salt-based desiccants (such as calcium chloride), but can be largely mitigated through proper material selection. Glycol-based systems have the disadvantage of atmospheric losses of glycol with the flue gas (Folkedahl and others, 2006). A combination of condensing heat exchangers with liquid desiccants is currently being investigated (Sarunac, 2010).

4 Dry scrubbers

Semi-dry FGD processes are the second most common FGD system installed on coal-fired power plants worldwide, with wet scrubbers being by far the predominant FGD technology. They typically consume around 60% less water than wet scrubbers, but more water than the sorbent injection processes.

The principal semi-dry processes in use today can be categorised as:

- spray dry scrubbers;
- duct spray dry process;
- circulating dry scrubbers.

All of these systems typically utilise a calcium-based reagent (calcium hydroxide) which is introduced as a slurry (spray dry scrubbers, duct spray dry process) or as a dry powder (circulating dry scrubbers). They are normally installed after the air heater. After passing through the semi-dry FGD system, the 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 SO_2 and SO_3 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 FGD system, unlike most installations in the USA. This enables the fly ash to be sold, and reduces the amount of waste for disposal. In addition, it can reduce the lime sorbent consumption (for a given desulphurisation level), prevent erosion of downstream equipment, and can help to achieve greater ESP efficiency (European Commission, 2006). Fly ash pre-collection, though, increases capital and O&M costs.

4.1 Spray dry scrubbers

Spray dry scrubbers (SDSs), also called spray dry absorbers, 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). SO₂ removal efficiencies are typically in the range 90–95%, depending on the sulphur content of coal. Lower SO₂ removal rates are attained when combusting high sulphur coals. 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% SO₂ removal efficiency (Sargent and Lundy, 2007). SO₃ removal efficiencies are ~99% (Moss, 2010), and over 95% of HCl, HF and oxidised mercury are removed when fabric filters are installed (Babcock & Wilcox, 2009; Tavoulareas and Jozewicz, 2005).

In the SDS process (*see* Figure 5), a concentrated lime slurry (a few systems use a sodium carbonate solution) 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 SO₃ in the downward flowing flue gas to form calcium sulphite and sulphate (*see* Section 2.1.1). Simultaneous cooling of the flue gas from 150°C or higher to as low as 17°C above the adiabatic water saturation temperature occurs (EPRI, 2007). The residence time of the gas in the scrubber is ~12–15 s. Part of the dry waste products is collected in the bottom of the scrubber and the rest from the flue gas as it passes through the particulate collector. A portion of these solids 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 (such as fly ash produced from subbituminous coal and lignite) will remove additional SO₂ and SO₃.

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.

Modern SDSs utilise a lime sorbent (hydrated or quick lime) since it is more reactive than limestone and is less expensive than sodium-based reagents. The hydrated lime is mixed with excess water on-site or the quick lime is slaked to produce a calcium hydroxide slurry containing ~20–25 wt% solids. The recycle solids are separately mixed with water to produce a slurry containing up to 45 wt% suspended solids (EPRI, 2007). Slaking quick lime requires relatively high quality water, whereas lower quality wastewater can be used when slurrying the recycle solids. The recycle slurry may be mixed with the fresh lime slurry before or during injection, or may be injected separately. Although recycling reduces the reagent cost, it increases capital and O&M costs.

 SO_2 removal efficiency is influenced by the coal sulphur content (SO_2 inlet concentration), inlet temperature, flue gas humidity, slurry droplet size and other factors. The rate at which the reagent slurry is fed to the atomiser directly influences the rate of SO_2 removal. Also, the amount of slurry that can be added is dependent on the amount of water that can be utilised. No more slurry can be injected when sufficient water has been added to cool the flue gas to the safe margin above the saturation temperature. This linkage between the rate of reagent slurry feed and the rate of water feed effectively limits the maximum rate at which reagent can be fed to the SO_2 scrubber. Thus the rate at which SO_2 can be removed is correspondingly limited (Jones and Weilert, 2011). Since most of the SO_2 capture occurs when the sorbent is still moist, adding deliquescent salts, such as chlorides, can improve SO_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 are considered to be efficient and reliable. Water consumption is $\sim 20-40 \text{ L/1000 m}^3$ of flue gas (European Commission, 2006) or $\sim 0.14 \text{ L/kWh}$ (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. Power consumption of SDSs is $\sim 0.5-1\%$ of the electric capacity of the power plant compared to

1–1.5% for wet scrubbers (European Commission, 2006). Installing a SDS to remove 90% of the SO₂ at the Big Stone Unit 1, in South Dakota, USA, would consume 3325 kW or 0.7% of nominal generation compared to 9500 kW or 2% of nominal generation for a wet scrubber removing 95% SO₂ (Otter Tail Power, 2009). SDSs can typically operate at loads of 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).

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\$ year 2009), or a unit cost of 297 US\$/kW, compared to US\$171,800,000 or 362 US\$/kW for a 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 than wet scrubbers due to their slightly lower sorbent utilisation (when achieving comparable SO₂ removal), higher sorbent costs and the costs of waste disposal. Possible applications of the waste products are covered in Section 2.3. 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, 2011). SDSs with fabric filters can capture more SO₃, HCl, HF and mercury than wet scrubbers, and with their smaller footprint, are usually preferable for retrofit.

4.2 Duct spray dry process

The duct spray dry process is essentially the same as the SDS process except that the lime slurry is sprayed directly into the ductwork upstream of the particulate control device. There is no separate absorber vessel. The ductwork should be capable of providing a residence time of 1 to 2 s to allow the moisture in the slurry to evaporate for the SO_2 removal reactions to occur and prevent undesirable deposits forming on the ductwork. In addition, the duct must not contain any flow obstructions (Srivastava and Jozewicz, 2001).

The process was developed primarily for retrofitting to existing power plants where a moderate degree of SO₂ removal (50–75%) is required and where plant operating hours and remaining lifetime are limited (DTI, 2000). Capital costs will be low since no separate absorber vessel is needed, and no process wastewater is produced. Drawbacks include the potential abrasion from the slurry, corrosion of the duct, and a low sorbent utilisation rate, as well as its relatively low SO₂ removal efficiency. SO₂ removal efficiency is lower than the SDS, circulating dry scrubber and wet scrubber systems, but generally slightly higher than the injection of a dry lime sorbent in DSI systems (*see* Section 5.3.1). Recycling the solid by-products can improve sorbent utilisation. Specialised processes and additives to improve the performance of the lime slurry sorbents have been developed.

Some power plants are injecting sodium-based sorbent solutions to capture SO_3 in what is essentially a duct spray dry process. This is discussed in Section 5.3.2, along with other dry and wet sorbents for SO_3 removal. The sorbents are discussed together so that they can be more easily compared.

4.3 Circulating dry scrubbers

The circulating dry scrubber (CDS) technology was first developed in Germany in the 1980s. Today,

Dry scrubbers

the total capacity of utility units worldwide using this technology is ~15,000 MW (Jones and Weilert, 2011), with units in Europe, Asia (particularly China), and the USA. Like SDSs, a CDS typically consumes around 60% less water than wet FGD processes (Bostick and Moss, 2011). It is fitted after the air heater and may follow a particulate collector which captures the fly ash. Unlike SDSs, a CDS normally utilises dry hydrated lime as the primary reactant in an upflow reactor in which the reactants are introduced through the bottom of the absorber. Ca(OH)₂ reacts with SO₂ to produce calcium sulphite. Some of the calcium sulphite then reacts with oxygen in the flue gas to produce calcium sulphate (*see* Section 2.1.1). The sulphite and sulphate compounds, along with the fly ash, if it is not pre-collected, and unreacted sorbent are removed by the particulate collector and continuously recycled via air slides to the scrubber to maximise sorbent utilisation. The fly ash contains a small amount of CaO which converts to Ca(OH)₂, increasing the reactant quantity. A small portion of the reaction by-products are removed to keep a constant inventory of solids in the system.

Dry fresh sorbent and water can either be added to the recycled solids or injected separately into the scrubber. Adding lime and water separately means that the lime feed can be easily adjusted to handle variable SO_2 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. In CDS systems, the injection water does not have to be of high quality since it evaporates during the process (Buecker and Hovey, 2011). Utilising low quality water, such as cooling tower blowdown or a wet FGD purge, could potentially lower the amount of wastewater to be treated and reduce water pollution from the power plant. Just enough water is introduced into the gas stream 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 (*see* Section 2.3). The reactions to remove sulphur can either take place in a fluidised bed (circulating fluidised bed scrubbers and gas suspension absorbers) or in an entrainment process (NIDTM).

The Enhanced All-Dry (EADTM) Scrubber, developed by Procedair (now Solios Environnement) in the 1980s, is a 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. The flue gas exits the tower and passes to the particulate collector. The process has been installed on industrial plants, but has not yet been installed on coal-fired power plants. 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.

4.3.1 Circulating fluidised bed scrubbers

Circulating fluidised bed (CFB) scrubbers (also termed circulating dry scrubbers) are in operation on facilities ranging in size from less than 10 MW to 350 MW. Multiple units are required for plants with a higher capacity, although some manufacturers claim that a single absorber can now be configured for 750 MW plants (Moss, 2010). China has some of the largest CFB units capable of capturing more than 90% of SO₂ when burning up to 3% sulphur coals (Sargent and Lundy, 2007). CFB scrubbers have been installed on Chinese coal-fired power plants up to 660 MW in size (Jiang and others, 2011). The largest CFB unit in the USA is at the 420 MW (385 MW net) Dry Fork station near Gillette, WY, burning PRB coal. The plant started commercial operation in Nov 2011, and uses a Graf-Wulff (now part of Foster Wheeler) reflux CFB scrubber, which was designed to reduce SO₂ by 95% down to 0.0258 kg/GJ (0.06 lb/million Btu) (Bostick and Moss, 2011). Performance testing achieved removal rates of >98% for SO₂, and >99% for SO₃ and HCl (Graf-Wulff, 2011). The Ca:S stoichiometric ratio is not given. Typical stoichiometric ratios of 1.5, 1.8 and 2 are required for 98% SO₂ removal when burning subbituminous (0.6% sulphur), low sulphur (1.3%) bituminous and medium sulphur (2%) bituminous coals, respectively (Sargent and Lundy, 2007). CFB systems have been successfully



Figure 6 CFB scrubber flowsheet for Dry Fork station (Bostick and Moss, 2011)

installed at plants firing high sulphur (3.5%) coals (Moss, 2010). SO₂ removal efficiencies as high as 99% (depending on inlet SO₂ loading) can be achieved, if high reagent consumption can be tolerated.

A flow diagram of the CFB system at the Dry Fork station is given in Figure 6. The flue gas enters the CFB reactor at the bottom and flows upwards through a bank of venturis. These increase the velocity of the flue gas before it mixes with the hydrated lime and recycled solids to create the characteristic fluidised bed. In some designs, such as the Graf-Wulff and Turbosorp®, the fresh sorbent and recycled solids are injected above the venturis, whereas the Lurgi Lentjes (now Doosan Lentjes) design introduces them below the venturis. Water is injected 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 reactor 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 two stages, with one level of water nozzles above the venturis and a second level further up the reactor. 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. SO₂ removal efficiency increased by over 1%, whilst the total water consumed was the same as that consumed in single stage humidification (Gao and others, 2010).

Sorbents that can be utilised without the need for flue gas humidification are being investigated at Tsinghua University in China. The sorbents are prepared by rapidly hydrating lime (CaO) with coal fly ash, CFB boiler ash or boiler ash. The product is then dried and crushed. The prepared sorbent consists of fine calcium-containing particles adhering to the surface of the larger ash particles.

Desulphurisation efficiencies of 67–83% were achieved in a pilot-scale CFB-FGD system at a Ca:S ratio of 2 and bed temperatures of 600–800°C. The desulphurisation efficiency was increased to 95% at a bed temperature of 750°C 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, 2010a,b, 2011; Matsushima and others, 2004; Zhang and others, 2006).

CFB scrubbers do not normally suffer from scaling, plugging or corrosion problems (DTI, 2000). They have good turndown capability and can accommodate rapid changes in fuel sulphur content. Their energy consumption is typically ~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. They consume around 60% less water than wet FGD processes. Water consumption at the Siekierki heating plant in Poland, fitted with a Turbosorp® scrubber, was contracted to be 125 L/min and energy consumption to be less than 750 kWh/h, with a SO₂ inlet concentration of 437–1260 ppmv dry (SO₂ outlet concentration \leq 175 ppmv, 6% O₂). The plant consumed 117 L/min of water and 520 kWh/h during the performance test when the SO₂ inlet concentration was 770 ppmv dry (SO₂ outlet consume 833 L/min (220 gal/min) of water when removing 98+% of the SO₂ (inlet SO₂ concentration is 1400 ppm or 1.38 kg/GJ (3.2 lb/million Btu)). It would consume ~2% of the power, and maintenance would cost 15 US\$/kW (Chenevey and Smith, 2011).

CFB scrubbers are easy to maintain as they do not require high maintenance mechanical equipment such as grinding mills and abrasion resistant slurry pumps (European Commission, 2006), and they generate no wastewater. As a result, CFB scrubbers have lower capital and maintenance costs and require a smaller footprint than wet limestone scrubbers. In addition, removal rates for SO₃, HCl and HF are greater in CFB scrubbers, and ~95% of mercury can be removed (Ake and Licata, 2011). However, they are more expensive to operate than wet limestone scrubbers due to their consumption of a more expensive reagent and they generate solid wastes that have little marketable value.

4.3.2 Gas suspension absorption process

The Gas Suspension Absorption (GSA) process was developed in Denmark by FLS Miljø (FLSmidth) and has been in commercial use since the 1980s in the power generation, waste-to-energy (municipal incinerators), iron and steel, and cement industries. A GSA system was recently installed at the Point Comfort power plant, TX, USA. The technology is typically applied to small- to medium-sized boilers burning low to high sulphur coals. SO₂ removal efficiencies of over 98% have been achieved, approaching those of wet scrubbers. Over 99% of the HCl and HF, and ~88% of the mercury is removed (Pittsburgh Energy Technology Center, 1996). Most of the SO₃ is also captured.

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 (*see* Figure 7). The flue gas enters the bottom of the reactor and passes through the venturi. A lime sorbent and cooling water mixture is 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). Rapid evaporative cooling occurs within the fluidised bed. 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. Small particles exiting the cyclone is around 3 to 5 s (Głomba and Mazurek, 2008).

Like CFB scrubbers, the GSA system does not normally suffer from scaling, plugging or corrosion problems, and it produces no wastewater. Water consumption at the 165 MW Skawina power plant in Poland is 14.2 m³/h (237 L/min) when treating 615,000 m³/h of wet flue gas. SO₂ removal efficiency was over 92% at a reactor inlet SO₂ concentration of 3600 m³ on dry flue gas (Głomba and Mazurek, 2008). Lime consumption is relatively low compared with other dry and semi-dry FGD processes. The



Figure 7 GSA process flowsheet (FLSmidth, 2010)

Ca:S ratio was 1.4 when 96% of the SO₂ was captured in a demonstration of GSA coupled with a pulse jet fabric filter. A 2.6% sulphur bituminous coal was combusted, and lime utilisation was ~70%. A lower SO₂ efficiency (90%) was achieved with an ESP. In this case the Ca:S ratio was 1.3 and lime utilisation was ~66%. The demonstration was carried out in the USA by the Tennessee Valley Authority on a 10 MWe slipstream in the 1990s (AirPol Inc, 1999; Pittsburgh Energy Technology Center, 1996). The GSA system is cheaper to install than wet scrubbers, but its operating costs will be higher due to the more expensive reagent. Pre-collecting the particulates in a cyclone reduces the particulate loading from the GSA system by 3–5 times compared to a SDS. The lower particulate loading, along with its small footprint, makes the GSA system especially suited for retrofit into an air pollution control system with an existing particulate collector. Like the other semi-dry processes, the dry by-products have little marketable value.

4.3.3 NID[™] system

Alstom's Novel Integrated Desulphurisation (NIDTM) technology (also known as 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, 2008), 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 NIDTM systems. The technology is generally limited to low to medium sulphur coals, where SO₂ removal efficiencies of up to 95% are required (EPRI, 2007). Nevertheless, improvements have increased this figure to 98%, nearer the efficiency achieved by wet FGD systems. The NIDTM installation at the 630 MW Brayton Point 3 power plant in Somerset, MA, USA, with a SO₂ inlet loading of 1.1 kg/GJ (2.5 lb/million Btu), is being designed to reduce SO₂ emissions by 98%. The Ca:S stoichiometric ratio is 1.5 to 1.8 (FGD & DeNOx Newsletter, 2012). NIDTM systems also remove SO₃, HCl, HF, and trace metals. SO₃ removal levels can reach less than 1 ppm (Alstom, 2012) and ~91% of mercury can be captured (Wu and others, 2008). Combining NIDTM with CFB bed boilers optimises desulphurisation when combusting high sulphur coals, and reduces reagent consumption. Limestone is injected into the boiler for SO₂ control. The unreacted lime (CaO) remaining in the fluidised bed boiler outlet flue gas helps remove SO₂ in the NIDTM reactor. For this application, the downstream particulate collectors are specifically designed to handle the very high circulating particulate loads (EPRI, 2007).

The unique feature of NIDTM 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, quick lime or alkaline ashes can be used as the reagent. Fresh reagent and the fly ash, reaction products and unreacted solids collected from the particulate collector are humidified in the mixer/humidifier by the addition of water (*see* Figure 8). When quick lime is used as the reagent it is dry slaked to Ca(OH)₂ (Alstom, 2008). The humidified Ca(OH)₂ mixture is then injected near the bottom of the NIDTM 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 as is the case in CFB scrubbers. The SO₂ reactions and drying times within the absorber take less than 2 s. The cooled flue gas then flows to the particulate collector, where the particles in the flue gas are removed and recycled back through the NIDTM system, and the cleaned gas is emitted through the stack.

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 μ m to less than 10 μ m. The large surface area created enables the reaction with SO₂ to proceed effectively within a short residence time (Buecker and Hovey, 2011).

Water consumption is about the same as for a lime spray dryer and CFB reactor. No wastewater is generated, and low quality water, such as cooling tower blowdown or a wet FGD purge, can be used in the humidifier/mixer (Alstom, 2008, 2012). One feature of NIDTM is its modular design, where each module can handle the equivalent of ~75 MW of flue gas. There is no upper limit on the number of modules that can be combined and so it can be installed on large power plants (Morris, 2010). An advantage with the modular design is its flexibility regarding unit downturn. A turndown of up to 50%



Figure 8 NID[™] process flow diagram (EPRI, 2007)

per module with no flue gas recirculation is possible for low load operation. The small footprint of a NIDTM module (<20% of a comparable spray dryer or CFB scrubber) makes it suitable for retrofit applications where space is limited. Capital investment costs are low.

4.4 Comments

The SDS and CDS semi-dry systems have a number of advantages over wet limestone scrubbers (Moss, 2010; Sargent and Lundy, 2007) including:

- the consumption of ~60% less water (but they consume more water than dry FGD systems);
- production of no wastewater as basically all the water added to the scrubber is evaporated. Therefore no wastewater treatment system is required;
- the waste products are dry and therefore easily handled;
- the scrubbers can be constructed of unlined low carbon steel as opposed to more expensive lined carbon steel or alloys used for wet scrubbers;
- smaller space requirement, and so may be easier for retrofit applications;
- lower auxiliary power consumption;
- more efficient capture of SO₃, HCl and other acid gases, and mercury;
- lower investment cost.

The main disadvantages of SDS and CDS systems when compared to wet scrubbers are:

- lower SO₂ removal efficiency although modern CDS systems can remove over 98% of SO₂, approaching the levels reached by wet scrubbers;
- multiple absorber vessels are typically required for units with a capacity higher than ~400 MW;
- no saleable by-product. The waste product has fewer uses than the saleable gypsum produced in wet scrubbing processes (*see* Section 2.3);
- higher operating costs mainly due to their higher reagent costs;
- maintenance costs of fabric filters in CDS systems can be higher than those for wet FGD units due to their greater wear. Higher particulate loading in the fabric filter from the recycling of by-products in CDS systems means more frequent cleaning and hence greater wear.

The characteristic features of SDS and CDS systems are given in Table 2. The SO₂ and SO₃ removal rates shown in the table are typical rates and will be site specific since they are partly dependent on the coal sulphur content. SDS systems are usually used at power plants burning low to medium (2%) coals, capturing up to 95% of the SO₂ (Moss, 2010). SDS technology is typically characterised as being limited to coals with sulphur contents below the equivalent of 1.29 kg SO₂/GJ (3 lbs of SO₂/million Btu). CDS technology is applicable to coals having a wider range of sulphur content, with over 98% of the SO₂ removed when firing high sulphur (3.5%) coals. Guarantees of 98% have been provided for coals with sulphur content (expressed as SO₂ emission potential) up to 3.1 kg SO₂/GJ (7.2 lb SO₂/million Btu) (Jones and Weilert, 2011). Both technologies remove over 95% of the HCl, HF and other acid gases, and nearly 99% of the SO₃.

A CDS normally utilises dry hydrated lime as the primary reactant in an upflow reactor in which the reactants are introduced at the bottom of the scrubber. This differs from a SDS which utilises a slurry reagent and the flue gas flows vertically downwards through the reactor. Since lime and water are added separately in a CDS, the lime feed can be easily adjusted to handle variable SO_2 concentrations during start-up, from load changes or if flexibility is needed in fuel selection. It 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. This hampers the ability of SDS technology to control emissions at low loads and prolongs the time during start-up before SO₂ removal can begin (Jones and Weilert, 2011). However, SDS has a more efficient turndown (Chenevey and Smith, 2011).

The injection water in CDS systems does not have to be of a high quality. Low quality process water could be used. On the other hand, high quality water is required if quick lime is slaked on-site for use

Table 2Comparison of SDS and CDS technologies (Chenevey and Smith, 2011; European Commission, 2006; Jones and Weilert, 2011; Sargent and Lundy, 2007)							
	SDS system	CDS system					
Absorber configuration	downflow reactor	upflow fluidised bed or entrained reactor					
Sorbent	Ca(OH) ₂ slurry prepared from slaked lime or hydrated lime fed into reactor via an atomiser	dry hydrated lime (Ca(OH) ₂) directly injected into reactor through venturis					
Water feed method	water included in slurry reagent	direct injection into reactor					
Recycle method	prepared as a slurry and fed via atomiser into reactor	air slide for dry feed into reactor					
SO ₂ removal, %	90–97	>98					
SO ₃ , HCI, HF, oxidised Hg,%	>95	>95					
Ca:S molar ratio	1.2–2	1.1–2					
Fuel flexibility	low to medium (2%) sulphur coals	low to high sulphur coals					
Sorbent products (dry)	$CaSO_3$, $CaSO_4$, $CaCl_2$ and fly ash	$CaSO_{3,}\ CaSO_{4},\ CaCl_{2}\ and\ fly\ ash$					
Residence time, s	2–15	5					
Water consumption	20–40 L/1000 m ³ flue gas (depends on gas temperature)	833 L/min (220 gal/min) (on a 205 MW unit)					
Power consumption, %	0.5–1	0.3–1					
Reagent consumption	lower than CDS (with recycle)	higher than SDS					
Pressure drop	lower than CDS	~10 cm (~4") water column higher than SDS					

in SDS systems. Nonetheless, low quality wastewater can be used when slurrying the recycle solids in SDS systems. SDS and CDS systems have equivalent water consumption (Chenevey and Smith, 2011).

Both the semi-dry systems recycle some of the solid by-product containing unreacted calcium hydroxide reagent to improve the calcium utilisation efficiency and minimise reagent use. The SDA technology must feed the recycle material through the atomiser as a slurry. Since the recycle slurry contains water, the rate at which it can be fed is restricted by the allowable total water flow to the SDS that will keep the flue gas exit temperature safely above the saturation temperature. On the other hand, CDS systems can achieve a high rate of solid recycle since the recycle material does not add any extra moisture to the flue gas. One consequence of the large solids circulation rate is the high dust loading on the fabric filter, and consequent wear. Thus CDS systems require more expensive and larger fabric filters than is the case for those associated with a SDS.

There appears to be little difference between the installed capital costs of SDS and CDS systems (Jones and Weilert, 2011; Sargent and 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 technology. An analysis by Jones and Weilert (2011) indicated that CDS technology requires 20% more reagent than SDSs. 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 equipment. The CDS technology generally requires a smaller number of motors than the SDS technology. 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).

5 Sorbent injection processes

As the name suggests, dry FGD systems typically do not require process water and consequently, do not produce a wastewater discharge stream. They therefore have the lowest water consumption of the various FGD systems, consuming no water, or a minimal amount if the sorbent needs hydrating or the flue gas is humidified to improve performance. Additional water may be consumed in the preparation of the sorbent, for example, during wet grinding. This chapter will discuss the dry sorbent injection processes. It includes the sorbent injection processes that consume minimal amounts of water, although these may be better categorised as semi-dry processes.

Dry sorbent injection systems have been in commercial use for more than 20 years. They were initially used for SO_2 control on small units burning low sulphur coals where wet FGD systems were not cost effective. More recently, they have been utilised in the USA for SO_3/H_2SO_4 mitigation to control stack opacity and reduce corrosion and fouling problems (*see* Chapter 2) as they remove SO_3 more efficiently than wet FGD scrubbers, as well as capturing HCl and HF. Currently there are around 60 units in commercial operation in the USA, although this is expected to increase with more stringent emission regulations coming into force (Bustard and others, 2011).

Sorbent injection systems can be classified into four types depending on where the sorbent is injected, namely:

- furnace sorbent injection;
- economiser sorbent injection;
- duct sorbent injection;
- hybrid systems. These are mostly a combination of the furnace and duct injection systems or may involve humidification of the flue gas (discussed in Sections 5.1 and 5.3).

In all the systems, the dry powdered sorbent is pneumatically transported to the injection lances and the resultant dry solid product is collected in the particulate control device (ESP or fabric filter), along with the fly ash. Fabric filters generally achieve greater SO_2 removal efficiencies than ESPs by virtue of the filter cake on the bags, which allows a longer reaction time between the sorbent solids and the flue gas. Sorbents used include calcium-, magnesium- or sodium-based reagents, ammonia or various proprietary sorbents. Some of these sorbents may be injected in slurry or liquid form. Injection as a solution or slurry generally requires longer residence times than dry injection since the reaction typically occurs after evaporation. In addition, slurries are more difficult to handle than dry sorbents. In some systems the sorbent is recirculated to increase its utilisation (regenerable), whereas others are once-through (that is, non-regenerable).

The effectiveness of sorbent injection is dependent on a wide range of factors, including the type of sorbent, sorbent particle size, sorbent residence time, sorbent dispersion, injection location, and system operating parameters, such as temperature. It is essential to have a good injection system to ensure that the sorbent and sulphur oxides are well mixed. The injection dispersion efficiency is influenced by the injection nozzle and lance design (Hopkins and Muoh, 2010). The type of sorbent and injection location is generally a function of the desired level of SOx control.

Figure 9 shows various sorbent injection locations. Some power plants will not have SCR units or wet FGD systems installed, whilst others have a hot-side ESP present. A hot-side ESP is located upstream of the air heater or SCR reactor. The following discusses some of the advantages and disadvantages of the different injection locations in relation to SO₃ control when a SCR unit is fitted.

Injecting the sorbent into the furnace and/or the duct between the economiser and SCR is only possible if the sorbent does not poison the SCR catalyst. Only the SO₃ formed in the boiler is removed. Adding sufficient excess sorbent to the furnace will remove the SCR-generated SO₃, but



Figure 9 Possible sorbent injection locations

only if the sorbent remains reactive both before and after the SCR. This is not the case for some magnesium-based sorbents, for example, and so a second injection location downstream of the SCR unit would then be required to remove the SCR-generated SO₃. Lowering the flue gas SO₃ concentration before it enters a SCR reactor can enable the SCR to operate at low unit loads and reduced SCR inlet flue gas temperatures without poisoning the catalyst by the condensation of ammonium bisulphate in the catalyst pores (Blythe, 2004). Injecting calcium- and magnesium-based sorbents can also protect against catalyst poisoning by removing vapour-phase arsenic (Benson and others, 2003). It is the preferred location if there is a hot-side ESP.

Sorbent injection into the duct between the SCR reactor and air heater removes both the boiler and SCR-generated SO₃. This minimises the possibility of ammonium bisulphate formation that could plug the air heater and foul downstream equipment, and the potential for sulphuric acid corrosion. It also allows the air heater to be run at lower temperatures, resulting in higher plant thermal efficiency (improved heat rate) and consequently, lower CO₂ emissions. But there may not be room to install the injection equipment in plants that have been retrofitted with an SCR system. An alternative location, such as between the economiser and SCR, would have to be employed (Moser, 2007). Injecting the sorbent between the air heater and particulate collection device can minimise the formation of visible SO₃/H₂SO₄ plumes. Corrosion of ESPs is also avoided, but ESP performance could be degraded if the sorbent adversely affects ash resistivity (as is the case for all injection locations upstream of an ESP). However, it would not prevent fouling of the air heater by ammonium bisulphate. Another injection location is between the particulate collection device and wet FGD system. This also minimises SO₃/H₂SO₄ plume formation and downstream corrosion, but would not protect upstream equipment. Unfortunately, particulate emissions may increase due to the sorbent reacting with SO₃ to form solids downstream of the particulate collection device (Biehn, 2011b; Kong and Wood, 2010; Ritzenthaler, 2007; Ritzenthaler and others, 2007).

Table 3 summarises the potential benefits of SO_3 capture for four different removal scenarios. The most benefits accrue on a coal-fired unit with an SCR system only if SO_3 is removed to a very low level (<3 ppm) upstream of the air heater. The amount of SO_3 reduction required to achieve the 3 ppm level under five scenarios with different combinations of fuels and SCR oxidation levels is given in Table 4. High sulphur coal is assumed to contain 3.5% sulphur. The table shows that, in all cases, a high removal efficiency (90–97%) is required. Even using a low oxidation SCR catalyst will only lower the required removal efficiency by a few percentage points.

Norman and others (2008) have provided a decision tree matrix to assist operators in selecting the appropriate sorbent and injection scenario for their plant. Real time, continuous measurement of SO_2 and SO_3 from power plant stacks could lead to a reduction in the sorbent injection rate, with consequent cost savings.

Table 3Potential benefits of SO3 removal under four scenarios for US plants (Moser, 2007)								
Removal scenario/benefits	Upstream of air heater (with 3 ppm maximum at air heater outlet and <1 ppm in plume)	Between air heater and ESP (with 5 ppm maximum in plume)	Between air heater and ESP (with 10–20 ppm in plume)	After wet FGD/wet ESP system (with <1 ppm in plume)				
Opacity/buoyancy benefits								
Protection against touchdown of visible plume trail	yes, absolutely	yes, absolutely	yes, very likely	yes, absolutely				
Ensure no visible plume discolouration or trailing plume	yes, absolutely	yes	no	yes, absolutely				
O&M benefits								
Protection from acid corrosion from air heater cold end to wet FGD inlet	yes, at all points	good, downstream of injection point	modest, downstream of injection point	no				
Reduce/eliminate air heater ABS fouling	yes	no	no	no				
Reduce air heater fly ash/SO $_3$ sticky deposits and fouling	yes	no	no	no				
Allow increased air heater heat recovery improve unit efficiency reduce gas volume (enhance ESP performance and reduce ID fan energy consumption)	yes yes	no no	no no	no no				
Allow modest increase in SCR NH ₃ with no ABS issue in air heater improve NOx removal generates saleable credits allow reduction in combustion NOx staging (reduces fireside corrosion)	yes yes yes	no no no	no no no	no no no				
Allow higher NOx removal at specific catalyst activity fewer catalyst replacements catalyst management flexibility (extend operation to outage)	yes yes	no no	no no	no no				
Allow reconsideration of SCR catalyst design (SO ₃ removal becomes economic variable) increase NOx removal/catalyst life with high activity catalyst allow catalyst design for very high Hg oxidation	yes yes	no no	no	no				
Reduce/eliminate ABS as factor in application of SNCR increase SNCR NOx removal (generate saleable credits) allow use of SNCR on higher sulphur coals allow possible offset of SCRs required in fleet	yes yes yes	no no no	no no no	no no no				
Assist in fly ash/carbon mercury removal allow increased Hg retention on fly ash improve Hg removal performance and economics for ACI	yes yes	yes, somewhat yes, somewhat	no marginally	no marginally				
Resolve SO ₃ issues for fabric filters	yes	yes	improves situation	no				
Reduce CO ₂ emissions via improved heat rate	yes	no	no	no				
ABS ammonium bisulphate; ACI activated carbon injection; SCR selective catalytic reduction; SNCR selective non-catalytic reduction								
Table 4SO3 reduction needed for a 3 ppm level at the air heater (Moser, 2007)								
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Scenario/fuel	High sulphur coal	High sulphur coal	High sulphur coal	High sulphur coal + petroleum coke	High sulphur coal			
SO ₂ to SO ₃ oxidation rate of SCR system, %	SCR system not in service	0.25	1	1.5	2			
SO ₃ level at SCR outlet, ppm	~30	~38	~60	~90	~90			
Required SO ₃ reduction, %	90	92	95	97	97			
Note: high sulphur coal is assumed to contain 3.5% sulphur								

5.1 Furnace sorbent injection

Furnace sorbent injection (FSI) is one of the simplest and cheapest commercial FGD systems to install, although operating costs can be high due to insufficient utilisation of the sorbent. The major cost is the sorbent itself; sorbent consumption is higher than in wet FGD processes. However, the addition of solids in the combustion area leads to boiler power reduction. FSI is best suited for use in small (<300 MWe) power plants (Zhou and others, 2010), that utilise low to medium sulphur coals, where only a moderate SO₂ removal efficiency is required, and for retrofitting in power plants where there is little space available in the unit area. Injecting calcium-based sorbents has the added benefit of capturing some HCl, HF and mercury (Hg).

FSI involves injecting a dry sorbent into the upper part of the furnace. An even distribution of sorbent across the furnace and adequate residence time at the proper temperature are critical for high SO_2 and SO_3 removal rates. A fine sorbent particle size increases SOx removal efficiency. Sorbent injection can be carried out at several levels within the furnace to deal with part load conditions and the target SOx reduction level. The reaction products, together with unused sorbent and fly ash, are collected in an ESP or fabric filter.

5.1.1 Sulphur dioxide

Commercially available limestone, dolomite (CaCO₃.MgCO₃) or hydrated lime are commonly used as the sorbent for SO₂ removal. The sorbents are injected into the furnace where the temperature is in the range 750 to 1230°C. Calcination of the sorbent occurs, producing reactive CaO which then reacts with SO₂ and SO₃ to produce calcium sulphate (*see* Section 2.1.1).

The upper temperature limit is determined by the thermochemical stability of calcium sulphate, which is unstable at temperatures above 1260°C. The lower temperature limit depends on complex interactions between sulphation kinetics, crystal growth and sintering, and the build-up of a barrier layer of CaSO₄ on the surface of the reactive CaO (European Commission, 2006). Sintering, for example, decreases the active surface area and porosity of the sorbent surface, and hence the sorbent reactivity. It is strongly affected by temperature, with sintering of calcined limestone rapidly increasing above 1100°C (Cheng and others, 2003). Reactions practically cease at temperatures below 750°C. In the optimum temperature range, the major SO₂ reactions occur within 1 to 2 s.

Slagging and fouling of heat exchangers by the reaction products can occur, so sootblowing may have to be increased. FSI also increases the amount of reaction products for processing and disposal. Operating at a Ca:S molar ratio of 2 with a 10% ash coal almost triples the rate at which the ash and spent sorbent must be collected by the particulate control device. Some retrofitted plants will require improvements in the ESP to accommodate such amounts (European Commission, 2006). In addition, the electrical resistivity of particulates increases substantially, degrading the performance of the ESP when FSI is applied to a boiler burning medium to high sulphur coals. Flue gas humidification or conditioning with SO_3 may bring the resistivity back to an acceptable level (Cheng and others, 2003). FSI can also increase the amount of carbon-in-ash (European Commission, 2006). Possible uses for the by-products are discussed in Section 2.3.

The SO₂ reduction achieved is site specific because of differences in boiler geometry, fuel properties, time-temperature history through the boiler, sorbent characteristics, injection configuration and other factors. A SO₂ removal efficiency of about 50% can be reached with a limestone sorbent at a Ca:S molar ratio of 4–5 (European Commission, 2006), whilst higher efficiencies can be obtained with Ca(OH)₂ (40–60%), dolomite (40–60%) and dolomite hydrate (50–65%) (Cheng and others, 2003).

By injecting finely ground (<1 μ m) limestone, the **ClearChem**TM process (EnerChem Inc) removes up to 84% of the SO₂ at a Ca:S ratio of 1.9, and virtually all of the SO₃. Pilot-scale and three short (1–2 weeks) boiler trials have been carried out and a demonstration-scale test is planned for 2013. Capital costs are estimated at US\$400,000 per unit, and operating costs at around 400–600 US\$/t SO₂ (Radway, 2012).





A FSI demonstration on a 188 MW tangentially-fired twin-furnace boiler achieved 40-55% SO₂ reduction with hydrated lime at a Ca:S ratio of 2.5. The highest reduction reached during the demonstration was 72% at a Ca:S ratio of 3.8 at a 70 MW load (Zhou and others, 2010). The difference in SO₂ removal efficiency between limestone and hydrated lime is illustrated in Figure 10. The figure also shows the relationship between SO₂ removal efficiency and temperature.

Higher efficiencies can be reached when water is sprayed into the flue gas duct before the particulate control device. This reactivates the unreacted sorbent that is still in the flue gas. It could be considered a hybrid system. The

water can be sprayed directly into the duct or via a separate reaction vessel. One such process is **LIFACTM** (Limestone Injection into Furnace and Activation of Calcium oxide), which has been installed on several coal-fired power plants worldwide. The process was developed in Finland in the 1980s and is available from Pollution Control Technologies (POCOTEC) (www.pocotec.com). Finely pulverised limestone is injected into the upper part of the furnace removing 25–35% of the SO₂. The flue gas, along with the reaction products and fly ash, passes through an activation reactor (situated between the air heater and ESP) into which water is sprayed. This humidifies the flue gas converting the lime into hydrated lime for further SO₂ removal and particulate conditioning. Recycling the dry solids removed from the ESP to the activation reactor increases the overall SO₂ removal rate to 75%, whereas recycling the solids as a slurry can raise the SO₂ removal efficiency to 85–90%. No wastewater is produced in the process. Instead some of the power plant's wastewater can be consumed in the activation reactor (POCOTEC, nd; Ryyppö and Ekman, 2000).

Critical parameters for the LIFACTM process include the flue gas temperature at the sorbent injection

location, residence time in the furnace, temperature of flue gas entering the activation reactor, droplet size of the water sprayed into the reactor, and residence time in the reactor. Both the flue gas temperature at the reactor inlet and the injected water droplet size affect the water evaporation rate in the reactor. A longer residence time in the reactor is required to evaporate larger water droplets (Srivastava and Jozewicz, 2001). A commercial demonstration test at the Whitewater Valley Station Unit 2 (65 MW) in Richmond, IN, USA, captured 70% of the SO₂ at a Ca:S molar ratio of 2.0–2.5:1 when burning 2–2.8% sulphur coal and with dry ash recycle. Extrapolation of the results suggested that up to 85% SO₂ removal is possible with appropriate selection of operating variables. The arsenic content of the ash by-product, though, could potentially cause problems (NETL, 2001). Otherwise the dry by-product can be used for road construction, landscaping, mine backfilling and other applications.

The **limestone injection multi-stage burner (LIMB) process**, where the sorbent is injected into the upper part of the furnace and the fuel through low NOx burners to additionally control NOx emissions, attained ~60% SO₂ removal with hydrated lime and ~40% with limestone, both at a Ca:S ratio of 2 and minimal humidification. SO₂ removal increased to 70% with maximum flue gas humidification. The demonstration tests were carried out on the 105 MW unit 4 at the Edgewater Station in Lorain, OH, USA using high sulphur (up to 3%) bituminous coal (NETL, 2000a).

Injecting the sorbent as a slurry, instead of a dry solid, increases sulphur removal by lessening sorbent sintering due to evaporation of the slurry droplets and by reducing sorbent particle size in the slurrying process (Cheng and others, 2003). But in this case some water is consumed in the preparation of the sorbent. A recent test at a bituminous coal-fired power plant in Pennsylvania, USA, removed 50-70% of the SO₂ when either a precipitated (at a SR of 1.3) or ground (SR 2.3) form of calcium carbonate was injected as a slurry. No adverse effects on fly ash capture in the ESP and its handling, or on furnace deposits occurred. The precipitated crystal structure of the calcium carbonate sorbent has a more open structure that allows the pollutants to access the core of the sorbent particles. It is best produced on-site or nearby because the structure limits the slurry solids to about 50%. The ground sorbent is milled to less than 1 µm for maximum reactivity and is injected as a 70-80% solid slurry. In future commercial applications, both types of sorbent will be injected at a 50% solids dilution level to maximise atomisation whilst keeping water inputs to a minimum in the furnace. Capture performance is expected to be enhanced if trace amounts of a non-toxic submicron catalyst is incorporated into the sorbent. Nozzle performance is key to achieving high capture efficiencies. Pilot combustor tests increased the SO₂ capture to 80% when testing a new nozzle design (Pastore, 2011).

A modification to the FSI process is the Ohio State Carbonation and Ash Reactivation (OSCAR) **process**, which creates a tailored mesoporous calcium carbonate sorbent from new or spent calcium sorbents. The sorbents are synthesised by hydration and carbonation in a slurry reactor in the presence of surfactants using power plant exhaust flue gas that contains nearly 15% CO₂. Calcium carbonate precipitates in the slurry, which is filtered and dried. Thus the process consumes some water. Laboratory tests indicated that the synthesised sorbent could improve sulphation by 20% compared to hydrated lime (Ca(OH)₂) sorbents; over 70% sulphation was achieved. A pilot-scale demonstration was carried out with sorbents synthesised from fresh lime or lime spray dryer ash using a slipstream of flue gas from the bituminous coal-fired boiler of the McCracken power plant, OH, USA. Sulphur capture for both sorbents under FSI conditions was limited. However, sulphur capture by sorbents that were allowed to pass through the system with heat removal down to ESP conditions was effective. Both types of sorbents showed nearly complete conversion in the fabric filter samples (Fan and others, 2005). Therefore fresh hydrated lime could be injected into the duct between the air heater and fabric filter, and the reactivated calcium carbonate sorbent injected into the furnace. Trace elements such as mercury, arsenic and selenium are also captured. Potential uses of the OSCAR solid by-products will be in the road and construction industry, mine reclamation, agricultural and other civil engineering applications (Fan and others, 2005; Taerakul and others, 2007).

APTECH Clean Stack Technologies (APTECH CST) technology (see www.aptechcst.com) is a

multi-pollutant hybrid system combining FSI with flue gas recirculation for the reduction of SO₂, SO₃, NOx, HCl and mercury. A calcium- or magnesium-based slurry is injected into the top of the furnace to control SOx emissions, along with urea to lower NOx emissions (also called selective non-catalytic reduction, SNCR). Recirculating flue gas extracted downstream of the particulate collector to the top of the furnace helps prevent slagging and fouling of the waterwall, superheater, and reheater. Pilot-scale tests at Southern Research Institute's 1 MW combustion research facility in Birmingham, AL, USA, reduced SO₂ and NOx emissions by ~48–75% (limestone sorbent), and ~50–74% (urea), respectively, when combusting subbituminous PRB coal. Burning bituminous Galatia coal (1.5% sulphur) achieved SO₂ and NOx reductions of ~55–60% and ~35–59%, respectively. The sorbents were tested separately. Optimising the injection locations and molar ratios for the sorbents, and possible synergistic effects with the combined injection of the two sorbents could lead to higher SO₂ and NOx reductions. SO₃ reduction was not measured in the tests, although modelling suggests nearly 100% of SO₃ could be removed. Injecting activated carbon could lower mercury emissions by over 60% (Kohan and others, 2008).

Sorbents with higher removal efficiencies that can withstand the high temperatures in the furnace are being developed. Sodium-based sorbents have a higher reactivity to SO_2 than calcium-based ones. However, pilot-scale tests found that injecting trona was less effective than limestone for corresponding Na:S and Ca:S molar ratios. Injecting a 20:80 trona:limestone mixture only achieved similar SO_2 reduction to those from limestone injection on its own (Western Research Institute, 2005). Sodium-based sorbents can also generate extensive fouling deposits.

5.1.2 Sulphur trioxide

Injecting sorbents into the furnace can remove SO_3 , which, as sulphuric acid, can corrode downstream equipment and lead to visible plumes (*see* Chapter 2). The pros and cons of FSI for SO_3 removal when a SCR unit is present were discussed at the beginning of the chapter.

Magnesium-based sorbents have an advantage over calcium-based ones $(CaO, Ca(OH)_2)$ since the former do not react with SO₂ at furnace temperatures and so SO₂ does not compete with SO₃ for reactive sites on the sorbent particles. A high ratio of injected calcium to SO₃ would be required to capture SO₃ with calcium-based sorbents. Furthermore, calcium oxide reacts with SO₃ to form calcium sulphate that can form hard deposits that are difficult to remove. The reaction product with magnesium oxide (magnesium sulphate) is water soluble and easily cleaned. In addition, magnesium oxide modifies coal ash fusion temperatures and slag properties, and so can reduce furnace slagging or make slag deposits more friable (Benson and others, 2003). When a SCR system is present, magnesium oxide reacts with ammonia to form ammonium magnesium sulphate, which again is water soluble and easily cleaned from downstream equipment. Nevertheless, a high SO₃ removal can increase the resistivity of the fly ash, impairing ESP performance. Some concern has also been expressed that injecting magnesium oxide or soluble magnesium-containing compounds can lead to a white coating of MgO/MgSO₄ on the furnace tubes, resulting in excess heat reflectivity (Fernando, 2003).

The effectiveness of four sorbents were tested at the Bruce Mansfield and Gavin power plants in the USA, namely dolomite, pressure-hydrated dolomitic lime slurry, a commercial magnesium hydroxide slurry and a magnesium hydroxide slurry by-product from a modified Thiosorbic® lime wet FGD process (Blythe, 2004). In the short term tests, a high SO₃ removal efficiency was only achieved with dry dolomite injection at high injection rates (a Ca:SO₃ molar ratio of ~40:1 for 90% removal measured at the economiser outlet). Only limited SO₃ control was attained when injecting pressure-hydrated dolomitic lime slurry. The excessively high molar ratios required for both of these sorbents to obtain the desired SO₃ removal level preclude their use, especially at plants that have ESPs because of the potential adverse effect on fly ash resistivity.

Over 90% SO₃ removal (based on ESP outlet concentration) was obtained at a Mg:SO₃ ratio of about 7:1 with the two magnesium hydroxide slurries. After injection, Mg(OH)₂ is heated, losing water of hydration to become MgO which reacts with SO₃ to form magnesium sulphate. The long-term (~25 day) full-scale tests showed that injecting magnesium hydroxide slurries could remove 90% of the furnace-produced SO₃/H₂SO₄ at a Mg:SO₃ molar ratio of ~3.5:1 (based on SCR outlet SO₃ concentrations) at the Gavin station which had an SCR reactor. When measured at the cold-side ESP outlet the overall sulphuric acid removal was only 70% at a Mg:SO₃ molar ratio of 5:1, with a maximum removal of ~78% at a molar ratio between 6:1 and 7:1. The two magnesium slurry sorbents gave similar results. There were generally no adverse effects on downstream equipment.

The long-term trials at the Gavin plant also found that the reactive $Mg(OH)_2$ remaining in the flue gas was relatively ineffective at removing SO₃ formed in the SCR, as the flue gas temperature downstream of the SCR unit is not high enough for the reactions to occur. This means that furnace $Mg(OH)_2$ injection alone is unlikely to achieve a high overall SO₃/H₂SO₄ control efficiency for power plants with SCR systems. A second sorbent injection system into the duct would be required.

A dual sorbent injection system is being installed on the 1400 MW unit at the Zimmer power plant near Moscow, OH, USA to achieve 90% overall SO₃ reduction (Benson and others, 2003). Magnesium hydroxide by-product (produced on-site from the Thiosorbic® wet FGD process) will be injected into the furnace at a rate of ~2.7 t (3 tons)/h, corresponding to a Mg:SO₃ molar ratio of 8:1, to remove 90% of the furnace SO₃. The injection rate may be lowered by optimisation of the injection locations. Hydrated lime will be injected into the duct before the ESP at a maximum rate of ~3.6 t (4 tons)/h to reduce SCR-generated SO₃ by 90%. This gives a molar Ca(OH)₂:SCR-generated SO₃ ratio of 7.7:1. The process is comparatively economical to install on plants that already use variations of the Thiosorbic® FGD process (EPRI, 2007).

Injecting a magnesium hydroxide slurry with 5–8 μ m sized particles into the furnace at Santee Cooper's Cross power plant (Units 1 and 2, each 600 MW) at Moncks Corner, SC, USA, has mitigated problems with furnace slag and SCR pluggage, as well as resolving the plume opacity problem. The SO₃ level was lowered by 66% at the air heater outlet. Additionally, improvements in heat rate (by 127 kJ (120 Btu)/kWh while utilising coals with a 2% lower heat content), boiler efficiency (by 0.65%), power capacity (44.5 MW increase) and fuel flexibility resulted. The injection system utilised Fuel Tech's Targeted In-Furnace InjectionTM technology. Ash sales to the cement industry were unaffected (Davis and others, 2008).

The operation and maintenance (O&M) costs associated with the injection of magnesium hydroxide are relatively high due primarily to the high sorbent cost coupled with the need for a high molar ratio for effective SO₃ reduction. Nozzle maintenance and the wear associated with pumping an abrasive slurry add to the O&M costs (Ritzenthaler and others, 2007).

5.2 Economiser sorbent injection

In this process, the sorbent is injected into the flue gas stream near the economiser inlet where the temperature is in the range 300–650°C (*see* Figure 9 on page 35). The most common sorbent is hydrated lime, when the optimum temperature range is between 500°C and 570°C. The Ca(OH)₂ reacts directly with SO₂ to form CaSO₃ (*see* Section 2.1.1) since the temperature is too low to dehydrate the Ca(OH)₂. A small portion (~10%) of the Ca(OH)₂ will decompose to form reactive CaO particles, which react with SO₂ to form CaSO₃ and some CaSO₄ (Srivastava and Jozewicz, 2001). The production of carbonate in the process is undesirable since it not only consumes the sorbent, but also blocks access of SO₂ to active sorbent surfaces. Carbonation increases with reaction temperature (Soud, 2000). SO₂ removal rates of ~20–50% have been achieved. Higher efficiencies can be obtained when fabric filters are installed. Economiser sorbent injection (ESI) is not currently in commercial use.

Water may be injected into the duct between the air heater and the particulate collector to increase SO_2 removal efficiency by hydrating any unreacted CaO. SO_2 removal efficiencies of up to 80% can be achieved (Srivastava and Jozewicz, 2001).

Laboratory experiments found that spent lime sorbent can be reactivated (that is, hydrated) by small amounts of water or steam in the temperature range of 100–200°C, and recirculated to improve the calcium utilisation efficiency. Water consumption is lowered by not producing a slurry. Sorbents treated by water had a higher SO_2 reaction activity than those treated by steam under the same temperature. The water activated sorbents achieved up to 30% calcium utilisation, whilst the steam activated ones attained 22% (Shi and Xu, 2005).

Injecting trona as the sorbent at the economiser inlet in a 90 MW boiler combusting bituminous coal (0.7% sulphur) removed over 50% of the SO₂ at a trona SR of 2.5. Decreasing the trona particle size from a D₅₀ of 30 to 13.7 μ m improved the SO₂ removal efficiency to 74% at a trona SR ratio of 3.5. Computational fluid dynamics (CFD) modelling optimising injection location and trona distribution indicated that 80% SO₂ reduction at a SR of 2.5 could be achieved, rising to over 90% at a SR of 3.5 (Cremer and others, 2008).

5.3 Duct sorbent injection

Duct sorbent injection (DSI) systems are in commercial use, removing SO_2 , SO_3 , HCl, and HF and enhancing mercury removal, depending on the sorbent used. The process involves injecting a sorbent evenly into the flue gas duct (*see* Figure 9 on page 35). Reaction with SOx occurs within the ductwork and the solid product is collected in the downstream particulate collector. When controlling SO_2 , the sorbent is usually introduced between the air heater and the ESP or fabric filter where the temperature is typically in the 120–180°C range. No dedicated absorber vessel is required, unlike most of the semi-dry and wet FGD processes. DSI is simple and easy to operate. It is more complicated than FSI but the removal efficiency is generally higher because the lower temperature in the duct allows a wider range of sorbents to be used.

Sorbents include hydrated lime, sodium bicarbonate, trona, sodium bisulphite and various proprietary sorbents. The performance of DSI is influenced by factors such as sorbent reactivity, quantity of injected sorbent, sorbent residence time in the flue duct, injection dispersion efficiency and operational parameters. A smaller particle size usually improves SO_2 and SO_3 removal efficiency and higher SOx removal efficiencies are usually attained with fabric filters, then with ESPs. Injecting sorbents not only increases the particulate load on the particulate collector system, but also the amount of by-products to be disposed of or sold (if possible).

5.3.1 Sulphur dioxide

The commercial sorbents used for SO_2 control are mainly calcium- or sodium-based and these can be injected dry or as a slurry or solution.

Calcium-based sorbents

Lime sorbents can lower SO₂ emissions by 50–60% (Srivastava and Jozewicz, 2001), but the low sorbent utilisation, due to the short residence time in the duct (0.5-3 s), is a drawback.

Most of the research on improving the performance of lime sorbents has focussed on increasing its surface area with additives. The reactivity of hydrated sorbents towards SO_2 is related to the sorbent surface area. The addition of inorganic hygroscopic salts, such as barium and calcium chlorides and sodium nitrates, can enhance Ca(OH)₂ sorbent performance (Ogenga and others, 2008). Reacting CaO/Ca(OH)₂ with fly ash, zeolites, rice husk ash or other pozzolanic materials can improve its

reactivity and performance. Pozzolans, primarily made of vitreous aluminous siliceous materials, react with Ca(OH)₂ to form complex hydrous calcium alumina silicates. The silicates have a high surface area and porosity and therefore a high reactivity. The sulphation reaction products are also stable (Maina and Mbarawa, 2011). Calcium utilisation of a CaO/fly ash sorbent (prepared by hydration at ambient temperature) was nearly three times higher than the original CaO particles (60% compared to 21%) after desulphurisation at 450°C. The calcium can be utilised more efficiently (82% utilisation rate) if the sorbent is recycled. Desulphurisation at a higher temperature (600°C) increased the calcium utilisation rate to 89% for the CaO/fly ash sorbent compared to 32% for the original CaO particles (Li and others, 1999).

 SO_2 removal increases with an increase in the amount of fly ash, up to a certain value which varies depending on fly ash composition, sorbent preparation conditions and other factors. Ogenga and others (2010) found that the highest SO_2 absorption capacity of 0.3336 of SO_2 moles retained per mole of sorbent was achieved at a CaO:fly ash ratio of 1:2. This compared to a maximum of 0.1823 moles of SO_2 absorbed on Ca(OH)₂ alone. The desulphurisation experimental conditions were similar to fabric filter conditions. An overview on the use of Ca(OH)₂/fly ash sorbents is provided by Ogenga and others (2008).

Lime/zeolite sorbents can enhance SO_2 absorption by over two times compared to lime alone. A 1:1 (by mass) lime/zeolite sorbent retained 0.26 moles of SO_2 per mole of sorbent, whilst 100% lime absorbed 0.127 moles of SO_2 (Maina and Mbarawa, 2011). Again, the experimental conditions were typical to those in fabric filters.

Higher SO₂ efficiencies have been achieved when Ca(OH)₂ was coated onto inexpensive expanded mineral supports, such as vermiculite and perlite. These expanded minerals have a large internal surface area and sponge like characteristics that allow the sorbents to carry a high amount of moisture (up to 35 wt%) that is needed for optimum SO₂ removal (Soud, 2000). An emission test achieved 70–75% SO₂ removal at a Ca:S ratio of 2 when injecting Fluesorbent (hydrated lime on expanded perlite substrate) at the Lausche heating plant at Ohio University in the USA. The target performance is 85–90% SO₂ removal at all loads when combusting bituminous coals with up to 4% sulphur. As a co-benefit, over 70% of the mercury was captured. The by-product can be used as a fertiliser (Harris, 2006).

Humidification of the flue gas facilitates SO_2 removal with lime sorbents. The water can be introduced either downstream or upstream of the sorbent injection point. The relative position of the dry sorbent and water injection point is optimised to maximise the impacts between the sorbent particles and water droplets. Although SO_2 removal efficiency increases as the saturation temperature is approached, the flue gas must be kept below this temperature in order to minimise deposits on ductwork and downstream equipment.

A demonstration of the **Coolside process** at the 105 MW unit 4 at the Edgewater Station in Lorain, OH, USA, using high sulphur (3%) bituminous coal achieved 70% SO₂ capture when hydrated lime was injected into humidified flue gas at a Ca:S molar ratio of 2. Injecting calcium-based sorbents can raise the resistivity of the ash, decreasing ESP performance. Humidification had the co-benefit of improving the performance of the ESP due to the conditioning of the particulates. A small amount of sodium hydroxide was included with the humidification water to enhance the lime-SO₂ reaction. Cheaper soda ash (Na₂CO₃) could be used instead of NaOH (NETL, 2000a). The presence of sodium-based compounds in the waste products, though, could be a drawback since they are water soluble (*see* Section 2.3).

Lime slurry can be directly sprayed into the duct, which does not require a separate humidification step. The slurry is atomised into very fine droplets (fine mist) to achieve a fast reaction time. It produces a more reactive sorbent, after the water has evaporated, compared to dry injection. This process is also termed duct spray dry process and is discussed in Section 4.2.

Sorbent injection processes

Water evaporation is an important design consideration with both slurry injection and flue gas humidification. The water must evaporate sufficiently to avoid formation of undesirable deposits in the duct and corrosion problems. This generally requires long, straight runs to avoid impaction on walls or elsewhere. Although lime slurry injection provides a slightly higher SO₂ removal than the injection of dry hydrated lime (Tavoulareas and Jozewicz, 2005), this advantage may be offset by the need for a somewhat more complex delivery system, and the potential for greater abrasion in the lime slurry system.

Instead of a once-through process, the partially spent sorbent can be recycled to the duct to improve sorbent utilisation and enhance SO_2 removal efficiency, and lower fresh sorbent costs. A pre-filter, if installed, has the advantage that the fly ash and desulphurisation products are collected separately. This makes recirculation of unreacted sorbent easier, and could allow the sale of the collected fly ash. Some processes recycle the spent calcium hydroxide sorbent after reactivation by hydration, which involves the consumption of small amounts of water. The Advacate process, for example, involves hydrating and mixing fresh calcium oxide in one step with recycled solids to form a slurry. The slurry is processed in a ball mill to expose fresh silica surfaces for reaction with hydrated lime to form a highly reactive, noncrystalline, calcium silicate slurry. Dry recycle solids are mixed with the fresh sorbent/recycle slurry to make a ~70 wt% by solids slurry and injected into the duct after the air heater. SO_2 removal of over 90% has been achieved (Srivastava and Jozewicz, 2001). The OSCAR process for reactivation of spent sorbents was discussed in Section 5.1.1. The process reactivates the unreacted calcium by converting it to calcium carbonate instead of calcium hydroxide.

Sodium-based sorbents

The injection of dry sodium bicarbonate and trona is practised at several power plants, principally in the USA. These sodium-based sorbents are more reactive than hydrated lime, and so no water is needed for flue gas humidification. Both sodium bicarbonate and trona are more reactive to SO_2 than sodium carbonate due to the 'popcorn' effect (*see* Section 2.1.2). The sodium-based sorbents, though, are more expensive than lime and limestone, and the recovered fly ash/sodium sulphate mixture has little economic value. The high sodium content makes it unsuitable for cement/concrete use. Sodium sulphate is water soluble and therefore its disposal is expensive and poses significant environmental challenges (*see* Section 2.3).

 SO_2 removal rates of 80–90% and 70–80% can be achieved with dry sodium bicarbonate and trona, respectively (VanDerWerff, 2011). Milling sodium bicarbonate and trona can increase their SO_2 removal efficiency. Less sorbent is required and hence cost savings can be made. However, the cost of milling on-site with the added cost of equipment and maintenance must be taken into account. Milling the as delivered trona from a 30–50 µm particle size to 10–14 µm reduces sorbent consumption by ~30%. For a 150 MW unit burning US Eastern bituminous coal and with 60% SO_2 removal, this equates to a reduction from 6.5 t (7.2 ton)/h of unmilled trona to 4.6 t (5.1 ton)/h for milled trona, resulting in an annual saving of US\$2,980,152 (when cost of trona is 200 US\$/t (180 US\$/ton)). For a 500 MW unit burning subbituminous coal and with 60% SO_2 reduction, trona consumption decreases from 6.8 to 4.8 t/h (7.5 to 5.3 ton/h), saving US\$3,193,020 per year (Day, 2010).

Both sodium bicarbonate and trona can also indirectly lower NOx emissions by around 10-25% without an SCR system (Maziuk, 2007). Sodium-based sorbents decrease the resistivity of fly ash and so can lead to an improvement in ESP performance. As with hydrated lime, mercury removal was enhanced by ~40% without activated carbon injection (ACI), and by over 90% with ACI at facilities burning bituminous coals. Injecting trona and activated carbon at the Dunkirk (530 MW) and Huntley (380 MW) power plants in New York, USA, reduced SO₂ emissions by over 55% and mercury emissions by over 90% (Clyde Bergemann, 2010). Another co-benefit is the removal of HCl and HF. Removing 50% of the SO₂ also captured 90% of the HCl, whereas the removal of 60% SO₂ increased HCl capture to 95%. The SO₂ and HCl concentrations in the flue gas before removal were around 700 ppm and 100 ppm, respectively, at a bituminous coal-fired power plant fitted with fabric filters (Campobenedetto and Silva, 2011).

However, some negative effects on mercury removal have been observed when trona is used for SO_2 removal (Maziuk, 2007). Care is required to avoid the formation of liquid sodium bisulphate (NaHSO₄), which is sticky at temperatures over ~185°C and so can deposit on the air heater and duct, causing buildup and plugging (Kong and Wood, 2010). Trona is more difficult to handle than hydrated lime or typical products due to its small particle size (~28 µm average particle size), its cohesiveness, affinity for moisture, and its temperature sensitivities. It needs to be very dry (<0.04% free moisture) for handling purposes (Ritzenthaler and others, 2007).

5.3.2 Sulphur trioxide

Injecting calcium- or sodium-based or other alkaline sorbents, either dry or wet, into the duct has been carried out commercially to remove SO_3/H_2SO_4 . DSI removes SO_3/H_2SO_4 more efficiently than wet FGD scrubbers and also captures HCl and HF. If the sorbent is injected downstream of the SCR then both furnace and SCR-generated SO₃ will be removed. Good mixing between the sorbent and flue gas is needed for high SO₃ removal efficiencies. Targeting only SO_3/H_2SO_4 removal when SO₂, HCl and other acid gases are present requires an understanding of the competing reactions, discussed in Campobenedetto and Silva (2011).

Calcium-based sorbents

A demonstration of the **CleanStack® process** on the Chesterfield 350 MW Unit 5 near Richmond, VA, USA, reduced SO₃ concentration at the ESP inlet by nearly half when ultrafine limestone $(2-3 \ \mu\text{m})$ was injected between the SCR reactor and air heater. Limestone injection rates were 136 kg/h (300 lb/h) and 227 kg/h (500 lb/h). CleanStack® promotes condensation of SO₃ on the ultrafine particles, and hence the condensation process does not depend on the composition of the particles, but only on the particle size distribution and concentration. Thus sorbents other than limestone could be used. A fabric filter and wet FGD system is being constructed to serve Unit 6 to enable the combustion of lower cost high sulphur coal. The gas temperature at the air heater outlet will be ~143°C (290°F). Consequently, SO₃ concentrations at the fabric filter inlet need to be reduced from the new level of 40 ppm to between 5 ppm and 7 ppm (achievable with CleanStack®). This would correspond to an acid dew point temperature between around 121 and 132°C (250 and 270°F), providing a sufficient temperature operating margin to eliminate concerns over damage to the fabric filter and its operating life, and blue plumes (Bowes and others, 2007; Evans and others, 2007). SO₃ concentrations at the ESP inlet ranged from 4.9 to 8 ppmv in the demonstration on Unit 5.

Dry hydrated lime is commercially utilised to lower SO₃ to the 5 ppm level (VanDerWerff, 2011). Over 80% reduction has been achieved when it was injected before the ESP (at a Ca:SO₃ mole ratio of 4.2:1). Injecting the hydrated lime after the air heater lowered SO₃ by 98%, when measured after the fabric filter, and used less sorbent than with ESPs. The filter cake on the fabric filter provided additional time and contact for the SO₃ to react with the sorbent (Biehn, 2011a,b). High surface area lime hydrate gives a better performance and creates less maintenance issues compared with low surface area forms (EPRI, 2007). Injecting hydrated lime reduces the potential to form sticky and corrosive ammonium bisulphate, provided enough SO₃ is removed, and has the beneficial effect of lowering HCl and HF emissions by ~25% (Wilson and Dickerman, 2009), and enhancing mercury removal. Mercury is adsorbed on active unburned carbon sites in fly ash. SO₃/H₂SO₄ competes with mercury for these sites and since the concentration of H₂SO₄ is substantially higher than that of mercury, fly ash capture of mercury is reduced. Injecting calcium hydrate before the air heater at a bituminous coal-fired power plant to lower SO₃/H₂SO₄ concentration from 7 to 3 ppmv increased mercury removal across the fabric filter from 30% to 58% (Campobenedetto and Silva, 2011). Mercury removal by fly ash can be enhanced by as much as ~40% (Biehn, 2011a).

The technology has relatively low O&M and capital costs (Ritzenthaler and others, 2007). Drawbacks include the high amounts of sorbent required for a high SO₃ removal and the adverse effects from high ash resistivity resulting from the injection of calcium-based sorbents on ESP performance. Some sites,

though, have had no problems with their ESPs. Blending sodium bicarbonate with lime can help minimise the ESP impact as sodium decreases fly ash resistivity. Humidification improves SO_3 removal performance of hydrated lime, but increases water consumption.

Magnesium-based sorbents

Around 60–70% of SO₃ can be removed when dry magnesium oxide is injected between the SCR and air heater at Mg:SO₃ mole ratios of 1:1 to 2:1, although >80% has been claimed (Blythe, 2004). Magnesium oxide also reacts with ammonium salts (from the SCR) to form ammonium magnesium sulphate. These deposits are friable and so can be removed with sootblowers. They are also water soluble making them easy to remove by water washing (Schmidtchen and others, 2002), although this may increase water consumption at the plant. Magnesium sorbents, though, may adversely affect downstream ESP performance by raising fly ash resistivity when a high amount of SO₃ is removed.

Injection of by-product magnesium hydroxide slurry (from a lime wet FGD system) ahead of a pilot-scale air heater lowered the SO_3 concentration from 30–55 ppmv (characteristic of high sulphur coal-fired units with SCR) to 10 ppmv or less at the air heater inlet at a molar ratio of 3 to 4. A 10 ppmv level is expected to lead to a stack SO_3 concentration of 5 ppmv or less due to incidental SO_3 removal across the air heater, ESP and wet FGD, thus greatly reducing or eliminating the visual plume opacity. No fouling of the air heater occurred (Benson, 2006).

Sodium-based sorbents

Sodium-based sorbents, such as sodium bisulphate and trona, have been commercially used to reduce SO_3 levels. They are more reactive than limestone and hydrated lime, due to the 'popcorn' effect (*see* Section 2.1.2). Some of the drawbacks of these sorbents are discussed in Sections 2.1.2, 2.2 and 2.3. As described earlier, injecting sodium-based sorbents can also enhance mercury removal and improve ESP performance. Injecting trona to remove 82% of SO_3/H_2SO_4 from the flue gas enhanced mercury removal by ~40% (Campobenetto and Silva, 2011). The trona was injected after the air heater at a bituminous coal-fired power plant with a cold-side ESP. Mercury adsorption can reach over 90% with activated carbon and trona injection (Maziuk, 2007).

Dry trona injection can capture over 90% of SO₃ at a stoichiometric ratio of ~1.5. It can be injected at almost any location in the gas stream where the flue gas temperature is between 135 and 815°C, with the higher temperatures resulting in better performance. Care, though, is required to avoid the formation of liquid sodium bisulphate, which at temperatures above ~185°C is sticky and can adhere to the air heater and duct surfaces (Kong and Wood, 2010). Figure 11 shows the SO₃/H₂SO₄ and flue gas conditions under which liquid sodium bisulphate (NaHSO₄) could form at equilibrium. Milling trona can reduce its consumption whilst improving SO₃ removal efficiency. The cost of milling



Figure 11 Conditions under which liquid sodium bisulphate could form (Kong and Wood, 2010)

on-site, though, must be balanced against the added cost of equipment and maintenance. A 700 MW unit with 50 ppm SO₃ in the flue gas removing 90% SO₃ (from 50 ppm) consumes 1.18 t (1.3 ton)/h of unmilled trona (30–50 μ m particle size) against 0.54 t (0.6 ton)/h of milled trona (10–14 μ m). An annual saving of US\$922,428 could be achieved with the milled trona, assuming trona costs 200 US\$/t (180 US\$/ton) (Day, 2010).

Solutions of sodium bisulphite and/or sodium sulphite, or sodium carbonate (soda ash) can be injected into the duct to control SO_3 emissions. The technology has been patented in the USA as the **SBS InjectionTM** technology. NOx and mercury can also be

reduced to some extent when SO₃ is removed. SO₃ removal efficiencies have ranged from 90% to over 98% at reagent stoichiometric ratios of 1 to 1.5 at US power plants, where the design SO₃ concentrations ranged from 42 to 110 ppm (Gray and others, 2008; Moser, 2007). Injecting sodium bisulphite at Na:SO₃ mole ratios in the range 1.5:1 to 2:1 can decrease sulphuric acid levels to <2 ppmv at the ESP inlet (Blythe, 2004). No adverse effects on ESP performance have occurred when removing sulphuric acid to these low levels, because of the conditioning effects of the sodium salt products formed in the process.

If the reagent is delivered as a solid (usually the case with sodium carbonate) or as a concentrated solution, then higher quality water (rather than low quality process water) is required to prepare the sorbent solution. The water must be low in calcium to avoid scale formation in piping and spray nozzles. The solution is sprayed through dual fluid nozzle into the duct to form fine droplets. The moisture rapidly evaporates and the resultant small particles $(1-10 \ \mu m \text{ in size})$ are very reactive; due to the 'popcorn effect' they have a high surface area (*see* Section 2.1.2). The dry reaction products (sodium bisulphates and sulphates) are collected in the particulate collector device. Since SO₂ is evolved into the flue gas during the reaction of sodium bisulphite and sulphite with SO₃ (*see* Section 2.1.2), a downstream FGD system is needed to remove it. Power plants injecting these solutions typically have a wet FGD system installed downstream of the ESP for capturing the SO₂.

The effectiveness of the process depends on good atomisation of the injected solution, good dispersion of the liquid into the gas, the amount of reagent used and the gas residence time (Moser, 2007). A longer section of duct downstream of the injection points is needed when injecting solutions instead of a dry reagent. This is to allow adequate time for water evaporation from the particles (~ 2 s) and to help prevent deposit formation on duct surfaces.

The sorbent solutions can be injected into the duct either before or after the air heater. Fouling of the air heater surfaces can occur at low Na:SO₃ ratios when sodium bisulphite/sulphite is injected before the air heater. Increasing the Na:SO₃ ratio to avoid deposition raises the operating costs. There is a concern that improper atomisation of the liquid sorbent will result in wetting of the duct surfaces, leading to corrosion and fouling of these surfaces. Improvements in the design of the injection nozzles and other maintenance practices have reduced the tendency for solids deposition on the ducts when injecting sodium sulphite, sodium bisulphite or sodium carbonate downstream of the air heater (Gray and others, 2005). Systems that inject the reagent upstream of the air heater have generally been more reliable than those injecting downstream of the heater (Moser, 2007).

Installed capital costs are commonly 5–10 US\$/kW (Moser, 2007). The O&M costs for the technology are relatively high (Ritzenthaler and others, 2007), with the reagent costs forming the largest component of the annual operating costs. A lower cost sodium sulphite/bisulphite reagent can be produced as a by-product from sodium-based or dual alkali wet FGD systems. Sodium carbonate is cheaper than sodium sulphite/bisulphite, and can lower operating costs by ~40–50% (Gray and others, 2005). A significant amount of compressed air is required for atomisation of the reagent solution. The feasibility of using high pressure hydraulic atomisation, which could reduce the operating costs by up to 20%, is being investigated (Moser, 2007).

Ammonia

Ammonia can be an effective method for removing SO_3 , especially for lower SO_3 concentrations (Ritzenthaler and others, 2007). Best results are obtained if ammonia is injected in the temperature range 150–200°C with a NH₃:SO₃ molar ratio in the range 1:1 to 2:1. Injection above 200°C results in the formation of semi-liquid ammonium bisulphate, which can cause fouling and corrosion of the duct and downstream equipment. Hence ammonia cannot be injected upstream of the air heater and so the air heater is not protected. A molar ratio of 1:1 produces mostly ammonium bisulphate, whereas a 2:1 ratio yields largely ammonium sulphate. Most plants operate at the higher molar ratios to avoid ash handling problems caused by ammonium bisulphate and because ammonium sulphate is the more desired product as it can be used a fertiliser. The molar ratio should not exceed 2:1 because this can

increase reaction with SO_2 and cause formation of ammonium bisulphite. In this environment, ammonium bisulphite forms submicron particles that cannot be removed by the FGD system and can produce a visible plume (EPRI, 2007).

Injecting ammonia between the air heater and ESP can remove 90-95% of the SO₃ at NH₃:SO₃ ratios in the range of 1.5:1 to 2:1, usually without affecting ESP performance (Blythe, 2004). As with all the sorbents, good initial mixing of ammonia with the flue gas is essential. Ammonia is used as a reagent for NOx control in SCR systems and for flue gas conditioning to enhance cold-side ESP performance by increasing fly ash cohesiveness. Consequently these plants already have a supply of ammonia on-site.

Tampa Electric have installed ammonia injection systems at the Big Bend station in Tampa Bay, FL, USA, where medium to high sulphur bituminous coal is combusted (Smolenski, 2008). The ammonia injection grid on Unit 4, consisting of 20 lances, is designed to inject 49 kg (109 lbs)/h of ammonia to mitigate a potential SO₃ concentration of up to 26 ppm at full load. Units 1 to 3 can inject 67 kg (148 lbs)/h to mitigate up to 32 ppm SO₃. Actual SO₃ concentration, though, have been lower than the calculated potential. The lances are located close to the air heater exit to give the injected ammonia a residence time of ~2 s before entering the ESP. An 85% SO₃ reduction has been achieved at Unit 4, where the SO₃ concentration of 20 ppm at the air heater outlet was reduced to 3 ppm prior to the entering the wet FGD system. This is below the 5 ppm level believed to cause opacity issues.

The biggest issue for ammonia injection is probably its effect on fly ash disposal and sales (*see* Section 2.3). The ammonia concentration in the fly ash at the Big Bend station ranged from 2200–3000 ppm, with an average of ~2500 ppm. The fly ash beneficiation process at the plant was modified to include an ammonia stripping process. This reduced the fly ash ammonia content below 100 ppm, allowing the continued sale of the fly ash (Smolenski, 2008). However, the stripping process increases water consumption at the plant. In addition, there is a risk of increased ammonia slip from excess ammonia that does not react with the SO₃. The ammonium sulphate particles formed from ammonia injection are submicron in size and can be difficult for the ESP to capture, leading to opacity problems. No change in opacity was observed from the Unit 4 ESP at the Big Bend station. But problems may occur at the other units where the ESPs are significantly smaller.

5.4 Comments

The sorbent injection systems have the lowest water consumption of the various FGD technologies, consuming no water or only a minimal amount if hydrated sorbents are used or the flue gas is humidified. They are simple to install and operate, and easy to retrofit with their small space requirements and short construction period. The systems are best suited for use in small (<300 MWe) power plants that utilise low to medium sulphur coals and where only a moderate SO₂ removal efficiency is required. More recently, DSI systems have been utilised for SO₃/H₂SO₄ mitigation on boilers up to 1300 MWe (Campobenedetto and Silva, 2011), as they remove SO₃ more efficiently than wet FGD scrubbers, as well as capturing HCl, HF and some mercury. This market is expected to increase in the USA where more stringent emission regulations are coming into force.

The capital cost and energy consumption of the sorbent injection systems are considerably lower than the semi-dry and wet FGD processes because they are simpler, consume less water (if any) and the dry residues are easier to handle and manage. Installed costs are around 8–12 US\$/kW for SO₂ control and 4–8 US\$/kW for SO₃/H₂SO₄ control (Campobenedetto and Silva, 2011), although Staudt and M J Bradley & Associates (2011) quote a higher figure of around 20 US\$/kW for a basic injection system with storage silo. The cost will be higher in cases where additional storage and materials handling are necessary. This is still substantially less than the capital cost for wet or dry scrubbers, which can reach 400 US\$/kW. The reagents used in the sorbent injection systems are more expensive than those utilised in wet limestone scrubbers, and they are not as efficiently utilised. This can contribute to a higher control cost in terms of cost per tonne of SO_2 reduced. The bulk of the operating cost is the price of the sorbent. In general, the calcium-based sorbents are cheaper than the sodium-based ones. The use of real time, continuous measurement of SO_2 and SO_3 in the power plant stacks could lower the sorbent injection rate, with consequent cost savings.

The different sorbent injection processes are compared in Table 5. The SO_2 and SO_3 removal rates

Table 5Comparison of different sorbent injection systems (Benson and others, 2003; Blythe, 2004; Cremer and others, 2008; EPRI, 2007; European Commission, 2006; Pastore, 2011; Srivastava and Jozewicz, 2001; VanDerWerff, 2011)									
Sorbent	Sorbent product	SO ₂ removal, %	SO ₃ removal, %	Comments					
FSI									
limestone CaCO ₃ hydrated lime	mainly CaSO₄ mainly	30–50 (slurry 70) 40–60		Calcium-based sorbents also capture furnace-generated SO_3 . Some HCl, HF and Hg also					
$Ca(OH)_2$ dolomite $CaCO_3.MgCO_3$	$CaSO_4$ mainly $CaSO_4 +$ MgSO ₄	(slurry 50–70) 40–60	<90 (furnace-	removed. Duct flue gas humidification increases SO_2 removal efficiency by ~10%. Boiler efficiency drops by 2%. Consumes 0.01–0.2% of electric capacity. Increases ash resistivity impacting ESP performance					
Mg(OH) ₂	mainly MgSO ₄		generated) 70 (SCR installed)						
ESI									
Ca(OH) ₂	mainly CaSO ₃	20–50		Not used commercially. Increases ash resistivity, impacting ESP performance. Duct flue gas humidification increases SO ₂ removal efficiency					
trona Na2CO3.NaHCO3.2H2O	Na ₂ SO ₃ + Na ₂ SO ₄	50–80		Decreases ash resistivity, may improve ESP performance. Spent sorbent/fly ash mixture has little economic value and can be expensive to landfill					
DSI									
Ca(OH) ₂	mainly CaSO ₃	50–60	>80	Enhances Hg removal. Higher SO ₂ removal when injected as a slurry or with additives or with flue gas humidification. Consumes 0.2% of electric capacity					
MgO	mainly MgSO ₄		60–70						
Na ₂ CO ₃	Na ₂ SO ₃ + Na ₂ SO ₄		90–98 (when injected as a solution)	Removal of HCI, HF, and some Hg. Decreases ash resistivity, may improve ESP performance. Spent					
NaHCO ₃	Na ₂ SO ₃ + Na ₂ SO ₄	70–90	>90	sorbent/fly ash has little economic value and can be expensive to landfill					
trona	Na ₂ SO ₃ + Na ₂ SO ₄	70-80	>90						
NaHSO ₃	Na ₂ HSO ₄ + Na ₂ SO ₄		90–98 (when injected as a solution)						
Na ₂ SO ₃	Na ₂ HSO ₄ + Na ₂ SO ₄		90–98 (when injected as a solution)						
ammonia	$(NH_4)_2SO_4$ or NH_4HSO_4		80–95	Effective at lower SO_3 concentration. Effect on fly ash sales and disposal					

Sorbent injection processes

given in the table are typical rates and will be site specific. For instance, a plant with fabric filters generally achieves a higher (\sim 5–10%) SOx removal efficiency than one with ESPs as the filter cake on the fabric filter provides additional time and contact for the SO₂/SO₃ to react with the sorbent. An even distribution of the sorbent across the boiler/duct and an adequate residence time at the proper temperature are critical for high SOx removal. Injecting dry calcium-based sorbents into the boiler or duct can lower SO₂ emissions by up to ~60%. A higher SO₂ reduction (up to ~90%) can be achieved when injecting dry sodium-based sorbents into the flue gas duct. Although ESI can achieve 50–80% SO₂ reduction, it is not currently in commercial use.

In most cases, SO₃ control efficiencies of 70% to 90% are required to appreciably lower, or completely eliminate, plume opacity due to the increased SO₃ concentration from the oxidation of SO₂ to SO₃ in the SCR unit. Magnesium hydroxide sorbents can capture nearly 90% of furnace-generated SO₃, but unless excess sorbent is present, FSI will not remove any of the SCR-generated SO₃. DSI is more efficient at removing both furnace- and SCR-generated SO₃, capturing over 90% with sodium-based sorbents or ammonia. The combination of Mg(OH)₂ slurry injection into the furnace with the injection of a second sorbent, Ca(OH)₂ into the duct can achieve ~90% SO₃ removal.

A drawback of the calcium-based sorbents is their poor utilisation and SOx removal efficiencies. Injecting the sorbents as a slurry, instead of a dry solid, into the furnace or humidification of the flue gas to reactivate the unreacted CaO can increase SOx removal by ~10%. These methods consume some water but typically produce no process wastewater. Slurries, though, are more difficult to handle than dry sorbents. The sodium-based sorbents are more reactive than the calcium-based ones and so flue gas humidification is not required; both sodium bicarbonate and trona are injected as dry solids. Sodium bisulphite, sulphite and carbonate are injected as solutions in an essentially duct spray dry process to remove 90–98% of the SO₃. Over the years a lot of research has been carried out on enhancing the performance of the calcium compounds and developing new sorbents. Developments in the use of zeolite sorbents for FGD have been reviewed by Liu and others (2010). But more research is needed before the sorbent injection processes can meet the SO₂ removal levels achieved by wet scrubbers.

Retrofitting a calcium-based sorbent injection system could degrade the performance of the ESP by decreasing ash resistivity. Flue gas humidification or conditioning with SO₃ may bring the resistivity back to an acceptable level. On the other hand, sodium compounds may improve ESP performance due to the increase in ash reactivity. However, trona is more difficult to handle than hydrated lime due to its small particle size (~28 μ m), cohesiveness and affinity for moisture. Care is also required to avoid the formation of liquid sodium bisulphate which can foul the duct and downstream equipment. Another concern with all sorbents is the effect of the collected spent sorbent on the saleability of the fly ash. Pre-collection of the fly ash may enable it to be sold. A drawback with the carbonate-based sorbents is the generation of CO₂ from the reactions with SO₂ and SO₃. This increases CO₂ emissions from the power plant.

6 Multi-pollutant processes

This chapter discusses pollution control systems that were designed as a multi-pollutant process, although in some cases the desulphurisation component can be installed separately. Research and development on numerous innovative multi-pollutant and FGD technologies have been carried out over the years. Some of these have reached the demonstration stage, whilst others are still at the laboratory- or pilot-scale. Technologies at the demonstration stage include corona discharge systems which are similar to the electron beam process (*see* Section 6.4). The main difference is that the high energy electrons are generated within the flue gas whereas the electron beam system generates the electrons externally. Pilot plant tests have achieved a removal rate of up to 95% for SO₂ and 50–70% for NOx using a pulsed corona discharge system with ammonia injection (Wu and others, 2003; Yan and others, 2006; Zhu, 2010). A demonstration unit on a coal-fired power plant in South Korea has been built. Although sometimes classified as a dry process, some water is utilised. For example, water vapour can be injected with the ammonia to improve SO₂ removal efficiency, or an aqueous ammonia solution is injected. In addition, the plasma reactor can be a dry or wet system.

Other technologies under development include removing up to 95% of SO₂ and 97% of NOx by microwave irradiation in a reactor containing ammonium bicarbonate (as a reducing agent) and a catalyst (Wei and others, 2011), reversible absorption processes using organic liquids that contain no water to remove SO₂ and CO₂ (Heldebrant and others, 2009), and membrane gas absorption using ionic liquids or other absorption solvents (such as sodium compounds). Some of these processes are discussed in Zhu (2010). Catalytic sorbents for multi-pollutant control are reviewed by Liu and others (2010). It is difficult to assess the water consumption of technologies at the early stage of development and so only commercial, or near commercial, multi-pollutant processes are discussed. The APTECH CST system (FSI with flue gas recirculation) is described in Section 5.1.1.

6.1 Activated carbon/coke process

The activated carbon or coke process is a dry, regenerable desulphurisation system that simultaneously removes SO_2 , SO_3 , NOx, mercury, HCl, HF and particulates. No water is added to the system as no flue gas humidification or saturation is required, and the sorbent is dry. As a result, only 1% of the water required by conventional wet FGD systems is used (Peters, 2010). The sorbent is regenerated, and a saleable by-product is produced.

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 the activated carbon/coke sorbents produced from scrap tyres (Wojtowicz and Serio, 2000) or palm shells (Sumathi and others 2010), coal tar pitch-based activated carbon fibres (Yoshikawa and others, 2005), and activated coke mixed with coal tar (Li and others, 2007). Activated carbon/coke impregnated with metals, such as calcium, cobalt, nickel, manganese or vanadium, can enhance desulphurisation (and denitrification) performance (Chu and others, 2010; Li and others, 2008; Sumathi and others 2010). 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).

Coal-fired power plants use activated coke as the desulphurisation sorbent. Although its surface area is less than conventional activated carbon, it is cheaper to produce. The activated coke process was developed by Berglau 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 use an advanced activated coke process for desulphurisation

(ResearchViews, 2011). This section will discuss the commercial ReACT[™] process marketed by J-POWER EnTech in Japan. More information can be found on their website (www.jpower.co.jp/entech_e/index.html).

6.1.1 ReACT™ process

The ReACTTM (Regenerative Activated Coke Technology) process has been installed on coal-fired units (up to 600 MW), sintering plants, incinerators and other industrial plants, mainly in Japan. 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 ReACTTM system is installed after the particulate control device.

The process consists of three stages, namely adsorption, regeneration and by-product recovery (*see* Figure 12). The adsorber is a single- or two-stage tower, depending on the design. It consists of a number of moving beds that operate in parallel. The flue gas enters through the side of the adsorber where it passes through the bed of activated coke that is moving slowly downwards. SO₂, SO₃, NOx and mercury are removed by the sorbent through adsorption, chemisorption and catalytic reactions. SO₂, for example, 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 also reacts with ammonia to form ammonium sulphate and bisulphate. Ammonia is injected into the duct upstream of the adsorber and into the regenerator to promote the removal of SO₂ and NOx. Particulates are reduced 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, heated and cooled. The adsorbed sulphuric acid and ammonium compounds in the activated coke decompose to SO_2 , N_2 and water, 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



Figure 12 ReACT[™] process (Peters, 2011)

years. This occurs everytwo to three years 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.

The SO₂-rich gas exits the regenerator and passes to the by-product recovery unit. Here, the SO₂ is converted into a saleable product, such as sulphuric acid 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 ReACTTM, low NOx burners, SCR and a second ESP installed after the ReACTTM system. Actual emissions are 2 ppm (0.0026 kg/GJ or 0.006 lb/million Btu) SOx, 7 ppm (0.0043 kg/GJ or 0.01 lb/million Btu) NOx, and 2 mg/m³ (0.00086 kg/GJ or 0.002 lb/million Btu) particulates. In addition, well over 90% of the mercury is removed. A demonstration of ReACTTM 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 and 97.1–99.6% mercury. Particulate emissions ranged from 0.003 to 0.0043 kg/GJ (0.007 to 0.01 lb/million Btu) (Dene and others, 2008b).

ReACTTM 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. In addition, 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 power consumption of ReACT is ~60% lower than a typical wet FGD (Peters, 2010). It consumes $\sim 0.7\%$ of the plant's gross output (Tavoulareas and Jozewicz, 2005), and has a good turndown capability. The performance of the adsorption process improves with lower flue gas temperature, so reduced temperatures from turndown or seasonal variations will improve 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). The system is easy to maintain, does not use water and can be adapted to meet limited space requirements. 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), and mercury can be recovered from the activated coke off-site. 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, and the disposal rate for the activated coke from the mercury zone in the regenerator would be <14 t/y (Peters, 2010). Unlike wet FGD processes, ReACTTM 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 ReACTTM, with its low SO₂, NOx and particulates 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.

6.2 Cansolv® technology

The first Cansolv® technology developed by Cansolv Technologies (now owned by Shell Global Solutions International) was SO₂ scrubbing, followed by a CO₂ capture system and then an integrated SO₂-CO₂ removal process. The Cansolv® SO₂ scrubbing system is a commercial, wet, regenerable FGD process that utilises a proprietary aqueous amine solvent to remove over 99.9% of the SO₂ (Cansolv Technologies, 2011). The process is suitable for high sulphur coals, and water consumption is low. The process has been used in a variety of applications including oil refineries, chemical plants, non-ferrous smelters and combustion gases (including treating flue gas from four 60 MW industrial cogeneration coal-fired boilers at a Chinese plant). The system will be installed on a new 1200 MW coal-fired power plant being built by China Guodian Corp at Duyun, China. The Cansolv® SO₂ scrubbing system will treat the flue gas from two 660 MW units in two parallel trains, each processing 2,600,000 m³/h. The SO₂ inlet concentration of 4000 ppmv will be reduced to <140 ppmv (Shaw, 2012).

The Cansolv® system (*see* Figure 13) is installed downstream of the particulate control device. The dedusted flue gas is first quenched to 30–60°C and saturated with water in the prescrubber section, which is located at the bottom of the SO₂ absorber. The flue gas then contacts the downward flowing amine solution over a section of mass transfer packing where SO₂ is absorbed. The treated flue gas exits the top of the absorber and is emitted through the stack. The SO₂-rich amine is pumped to the regenerated by indirect steam stripping and is returned to the absorber via the lean/rich amine heat exchanger for energy recovery. The lean amine solvent is regenerated by indirect steam stripping and is returned to the absorber via the lean/rich amine heat exchanger and lean amine cooler. While low pressure steam is the most common stripping agent, and will be used at the Duyun power plant, other sources of energy could be used depending on their availability and relative value to the operator. A slipstream of the lean amine is purified to prevent accumulation of heat stable salts formed from strong acids in the flue gas.

A portion of the lean amine from the regeneration column enters a reboiler where part of the water in the solution is vaporised to serve as the steam source for the regenerator. At the Duyun power plant, the gas exiting the top of the regenerator passes through a heat recovery unit (as the steam value is high) before water is removed by condensation and returned to the top of the regenerator as reflux. In applications where the steam value is low, the heat recovery unit is omitted. SO₂ is recovered as a pure, water saturated by-product which can be converted into various sulphur products, such as sulphuric acid (fertilisers) or sulphur. If sulphuric acid is produced, then 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 Cansolv® system (Cansolv Technologies, nd; Just and Shaw, 2008).

This is one of the most efficient SO₂ removal technologies, removing over 99.9%, resulting in emissions as low as 10 ppmv (Shaw, 2009). However, only ~50% of SO₃ is captured and therefore a SO_3 removal system may be required to meet strict SO_3 emission regulations. This can be achieved by processes such as the injection of sodium-based or other sorbents into the ductwork (see Section 5.3.2). Water consumption is low primarily because it is a regenerable system. The aqueous 25 wt% amine solvent is continuously circulated between the absorption and regeneration units. Therefore the main source of water loss in the system itself is the small make-up that is required (typically less than 15% of the solvent initial fill per year) plus any mechanical losses or spills. The other source of water loss is the small 'bleed' from the prescrubber section of the absorber tower where the flue gas is quenched. The Cansolv® system does include some water recovery features. Most of the water is removed from the SO₂-rich gas leaving the regenerator, and is returned to the top of the column. Furthermore, heat recovery in the lean/rich amine scrubber reduces both the amount of steam necessary to regenerate the solvent and the amount of cooling water needed to cool the lean solution to absorber conditions. Cansolv® consumes less than 1 t of water for each t of SO₂ removed, assuming a 60°C flue gas temperature and an inlet SO₂ concentration of 3000 ppm (Shaw, 2012). This figure does not include the water consumed in quenching the flue gas to 60°C. Energy consumption is low (Hakka, 2007), the footprint is smaller than a wet FGD system, and a saleable by-product can be produced from the recovered SO₂. A small quantity of liquid wastes is produced from the amine purification unit and elsewhere.

An integrated SO₂-CO₂ system has been developed whereby SO₂ is first removed using a SO₂ scrubbing system followed by a CO₂ capture unit that removes ~90% of the CO₂. Thus two different liquid loops (one each for the SO₂ and CO₂ systems) are required. About 70% of the heat used for SO₂ stripping is recycled for CO₂ stripping, thus reducing unit CO₂ capture costs. A water wash system is utilised for CO₂ removal in the absorption column (Cansolv Technologies, nd). Water consumption is site-specific. In one case study, it was found that a Cansolv® CO₂ capture unit would consume around 53 L 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). The integrated SO₂-CO₂ Cansolv® system is being installed at the 150 MWe Boundary Dam project in Estevan, Saskatchewan, Canada, with planned operation in 2014. The SO₂ product will be used as a feedstock by the local fertiliser industry and the captured CO₂ for enhanced oil recovery in the nearby oil fields. More information about the technologies can be found on Cansolv Technologies Inc's website (www.cansolv.com).

6.3 CEFCO process

The CEFCO (Clean Energy and Fuel Company) process is a wet regenerable system that sequentially removes trace metals (including mercury) and fine particulates, SOx, NOx and CO_2 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 incineration facilities to control hazardous waste emissions. 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 CO_2 are produced. Since the CEFCO process is designed as a modular system, the

SOx removal module could be independently installed if just FGD is required. Removal efficiencies of over 99.9% for mercury, fine particulates, SOx and NOx and at least 90% of CO_2 are claimed. Water conservation is optimised, and with water vapour condensation and water recovery, the CEFCO process is a net generator of water. The process is currently being tested at a pilot plant (1–3 MWth) at the Peerless Manufacturing Co's industrial facility in Wichita Falls, TX, USA.

The CEFCO modules are installed downstream of the ESP/fabric filter. The flue gas (*see* Figure 14) 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. Secondly, they shatter the reagent droplets into very small (µm) droplets, which rapidly react with the target pollutant molecules. 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 rapidly expand into a sub-atmospheric zone, allowing the small droplets to grow in size through repeated collisions, nucleation, agglomeration and moisture condensation. Simultaneously, rapid chemical reactions with the pollutants occur, encapsulating the reaction products within the droplets. The droplets are then stripped from the flue gas in the aero-coalescer (gas/liquid separator) and the resultant liquid is sent to the product tanks for processing into saleable products. The flue gas 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 (Cooper and others, 2010; Tang, 2011; Tang and Sanyal, 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 (K_2CO_3 or Na₂CO₃) is used as the reagent, enabling saleable products to be made. The molar ratio of the hydroxide reagent to SOx is around 1–1.05.

The liquid from the aero-coalescer in the SRS module contains potassium sulphates, sulphites and bisulphites, along with potassium carbonates and bicarbonates (with a potassium carbonate and potassium hydroxide reagent solution). The liquid is first decarbonated by steam heating, before it is oxidised with air to convert the sulphites into sulphates. Potassium sulphate is recovered by evaporation and crystallisation, and sold as a fertiliser. The liquid left is principally potassium carbonate, which can be recycled (Cooper and others, 2010).

The process utilises a slipstream of the 'waste steam' leaving the last turbine that is returning via the return-loop to be condensed. Between 3 and 6 wt% of steam at a pressure between 0.69-2.76 MPa (100–400 psig) is required to generate the shockwaves (Tang, 2011, 2012). This steam can be considered as 'borrowed water' since the CEFCO process is a net generator of water. 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.

The CEFCO process can be considered a low water multi-pollutant system since it generates water, which can be recovered and recycled within the power plant. Water is produced (Tang and Sanyal, 2010) through:

- the reactions of the hydroxide reagent solution with CO₂ resulting in bicarbonate/carbonate that is recovered after exiting the aero-coalescer;
- the water input in the chemical feed stream which is recovered through condensation from the liberated and concentrated CO₂ gas stream during the decarbonation and recovery step;
- capture of the moisture condensed from the flue gas itself and the stack gas.

A material balance carried out for a 1000 MW power plant employing all four modules estimated that 3886 t/MWe (4284 ton/MWe), 2941 t/MWe (3242 ton/MWe) and 2819 t/MWe (3108 ton/MWe) of water would be produced when burning US lignite, subbituminous and high sulphur bituminous coals, respectively. The average energy consumption of each of the four CEFCO modules would be 57 MW when firing lignite, 25.5 MW for the subbituminous coal, and 32.5 MW with the high sulphur bituminous coal (Tang, 2012). Thus the full four-module multi-pollutant system would have an energy penalty (parasitic load) of 22.8%, 12.4% and 13% for the lignite, subbituminous and bituminous coals, respectively. The parasitic load could be excessive for plants firing lignite.

The reactions within the aerodynamic reactors take place within seconds and so the equipment footprint is small. The SRS module is smaller than a wet limestone FGD unit. The CEFCO technology could be retrofitted or applied to new power plants. It 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 capital (CapEx) and operating expenditure (OpEx) costs for a 1000 MW plant (with all four modules) firing lignite, subbituminous and high sulphur bituminous coals are estimated to be US\$1382 million, US\$1069 million and US\$1921 million, respectively. Each module produces saleable products to generate revenue. The CapEx and OpEx costs for just the SRS module are around US\$275 million and US\$62 million, respectively, and the module could generate a revenue of US\$208 million per year when utilising subbituminous coal. However, if the process (all four modules) is operated in a 'capture-only' mode, without the production of saleable products, then the reagent component of the OpEx costs can be reduced by using cheaper calcium-based reagents instead of potassium-based ones (Tang, 2012). More information about the process can be found on CEFCO's website (www.cefcoglobal.com).

6.4 Electron beam process

Although the electron beam process is a dry scrubbing process that simultaneously removes SO_2 , SO_3 , NOx and other acid gases, water is consumed in the conditioning of the flue gas and elsewhere. Over 95% of SOx and up to 75% of NOx can be removed. The electron beam-flue gas treatment (EB-FGT) process has been demonstrated on two coal-fired plants in China, and one in Poland, and a few other industrial plants.

Dedusted flue gas is cooled and humidified, typically in a spray cooler. Ammonia is added as an aqueous solution to the spray cooler or separately after the spray cooler (as a gas). The low temperature (65–80°C), wet (10–15% humidity) and ammonia-rich flue gas enters an irradiation reactor, where high energy electrons react with molecules in the flue gas to produce radicals that then

react with the SOx and NOx in the flue gas to produce sulphuric and nitric acids, respectively. These acids, in turn, react with the ammonia to form ammonium sulphate and ammonium nitrate. The ammonium salts (ammonium sulphates and nitrates) are collected in a downstream ESP, and sold as fertiliser. The chemical reactions are completed within seconds.

Depending on process conditions, ammonia water consumption was in the range of 150–600 kg/h at the Polish facility in Pomorzany (Hiete and Schulte-Beerbühl, 2012). Cooling water is also needed to cool the reaction unit. A 65 MW boiler with a flue gas flow of 300,000 m³/h and removing 98% of the SO₂ with electron beams consumes 108 t/d of water and 48,000 kWh/d (48 MWh/d) of electric power (PlasTEP, 2011). The process material balance carried out by PlasTEP found that the EB-FGT process (based on Polish data) consumes more water than a wet limestone FGD + SCR system, when treating 1000 m³ of flue gas. Therefore this process will not be discussed any further.

6.5 EnviroScrub

EnviroScrub, developed by Enviroscrub Technologies, is a 'closed loop', regenerable sorbent system capable of removing SO₂, SO₃, NOx, mercury and particulates. The technology is based on the PahlmanTM process, and is installed after a particulate removal device. It has only been tested at pilot-scale at a few coal-fired units when over 99% SO₂, 98% NOx, and up to 99% elemental and 84% oxidised mercury were removed (Hammel, 2004).

The Pahlmanite sorbent is made up of manganese oxides and is injected, either dry or as a concentrated slurry, into a reactor, such as a spray dry absorber or fluidised bed. SOx and NOx react with manganese oxide to form manganese sulphates and nitrates, respectively. Mercury is oxidised and absorbed on the sorbent. The spent (and unused) sorbent is then collected in the downstream fabric filter, and the clean flue gas is emitted through the stack. The spent sorbent is regenerated using a wet chemical system. It is mixed with water and transported to the regeneration vessel where it is contacted with a hot, oxidising, aqueous solution, which dissolves the manganese sulphates and nitrates. The chemical composition and operating conditions of the regeneration vessel are controlled so that the dissolved manganese is precipitated to form fresh sorbent. In addition, the remaining solid sorbent is re-oxidised and re-activated. The solution containing the sulphate, nitrate and mercury compounds is treated to remove mercury and any chlorides, and the resulting sulphate and nitrate solution (or solids if required) can be sold. Some of the sulphate containing solution can be treated to produce the oxidant for use in regenerating the Pahlmanite sorbent (Hammel, 2004; Tavoulareas and Jozewicz, 2005).

Although the sorbent can be injected dry, water is consumed when regenerating the sorbent. Since the amount of water consumed in the process could not be ascertained, the technology will not be discussed any further.

6.6 SNOX[™] process

SNOXTM (previously called WSA-SNOX) is a regenerative, catalytic process, developed by Haldor Topsøe, to control SOx and NOx emissions. It consumes no water and produces a saleable sulphuric acid by-product (Lindenhoff, 2011). Large SNOXTM units are in use on a 300 MW coal-fired power plant in Denmark (since 1991), a petcoke-fired power plant in Italy, and a heavy residual fuel oil power plant in Austria. Over 55 small-scale units, including some that operate with just the desulphurisation step, are operating worldwide treating a range of sulphur containing offgases. SNOXTM 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, 2000b). The process is designed for high sulphur fuels. Up to 99% of SO₂ and SO₃, up to 96% of NOx and essentially all the particulates are removed (Schoubye and Jensen, 2007). The SNOXTM unit is located downstream of the particulate control device. The dedusted flue gas (*see* Figure 15) is reheated in a heat exchanger to ~400°C and ammonia is injected before the gas enters the NOx reduction reactor. Here NOx is catalytically reduced by ammonia 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. Later designs have integrated the two catalytic reactors into a single vessel. 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 Sulphuric Acid) condenser.

The flue gas needs to be cleaned to below 2 mg/m^3 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 10 years can be expected (Halder Topsøe, 2006; Schoubye and Jensen, 2007). 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 2000b). The efficiency of the SO₂ to SO₃ oxidation determines the SOx emissions since all SO₃ is hydrated.

No water is consumed in the SNOXTM process and hence no waste water is produced. In addition, no waste products are generated, only very low quantities of catalyst degradation fines (NETL, 2000b). 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-Beerbühl, 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. The cooling air discharged from the WSA condenser can be used in the boiler as combustion air. It was estimated that for a 500 MW coal-fired power plant, the heat recovery is more than the supplemental power needed for the SNOXTM plant, and could provide a potential net gain equivalent to 8 MWe (NETL, 2000b). Even before credits for sulphuric acid sales, the operating

Figure 15 SNOX™ process (Lindenhoff, 2011)

cost of SNOXTM units decreases with increasing SOx content in the flue gas due to heat recovery (Halder Topsøe, 2006; Schoubye and Jensen, 2007). SNOXTM has lower capital requirements and lower operating and maintenance costs than a wet limestone FGD + SCR plant burning high sulphur coals (NETL, 2000b). Treating low and medium sulphur coals, though, will cost more than a wet limestone scrubber (Lindenhoff, 2011). Unlike wet scrubbers (*see* Section 3.1), SNOXTM generates no CO₂. Flue gas with up to 1 vol% SO₂ can be treated. Higher SO₂ concentrations would require modifications to the plant layout (Halder Topsøe, 2006). However, SNOXTM requires more space than a typical wet FGD or SCR unit (NETL, 2000b).

6.7 SOx-NOx-Rox Box process (SNRB™)

SNRBTM is a dry process that removes SO₂, NOx and particulates in a high temperature catalytic fabric filter (baghouse). The system operates at a temperature of ~425–455°C and is located before the air heater. SO₂ is removed by injecting either calcium- or sodium-based sorbents into the flue gas (DSI, *see* Section 5.3). NOx is removed via SCR. Ammonia is injected into the flue gas upstream of the fabric filter, and the SCR catalyst is incorporated in the fabric filter. The particulates, including the spent and unused sorbent, are removed by the fabric filter bags.

In 1992-93, the SNRBTM system was demonstrated on a 5 MW slipstream (1000 m³/h flue gas) at the RE Burger power plant, OH, USA, burning bituminous coal (3.5% S). SO₂ removal efficiencies of 80–90% were achieved at a Ca/S molar ratio of ~1.8–2, whilst SO₂ removal was >90% with sodium bicarbonate injection. NOx removal was >90% with an ammonia slip of less than 5 ppm. Over 99.9% of particulates were captured (US DOE, 1999; NETL, 2000c; Tavoulareas and Jozewicz , 2005).

SNRBTM has a small footprint, and is simple to operate. No water is consumed in the process. Since SO_2 and particulates are removed before the air heater, 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. The capital and operating costs of a SNRBTM system are expected to be lower than a system incorporating separate wet FGD, SCR and particulate removal components. However, it may not be an economic choice for applications requiring SO_2 removal over ~85% (US DOE, 1999). Since the small-scale RE Burger demonstration in the mid-1990s, the technology does not appear to have been developed any further or tested at a larger scale.

7 Conclusions

A wide variety of FGD technologies are available for controlling SOx emissions that vary in the amount of water they consume. Technologies with a low water usage are important because of the large number of FGD systems being installed in response to tightening emission regulations. Reducing water usage is particularly important in arid regions of the world and in areas subject to drought. There is therefore a need for FGD systems that meet the following criteria:

- low water consumption;
- high SO₂ and SO₃ removal efficiency;
- high reliability;
- low capital, operating and maintenance costs;
- low auxiliary power consumption;
- saleable or usable by-product.

Limestone wet scrubbers, the most common FGD system for controlling SO₂ emissions, can remove over 98% of SO₂, have a high reliability and produce saleable gypsum. Auxiliary power consumption is around 1.2–2%, depending on the coal sulphur content. However, they increase a plant's CO₂ emissions (CO₂ is a by-product of the desulphurisation process) and require large supplies of water. Wet scrubbers are responsible for around 10–15% of the evaporative water losses in coal-fired power plants equipped with water cooling systems. The figure is considerably higher in plants employing dry/air cooling systems where wet scrubbers account for 40–70% of total site water usage. Technologies to reduce the water losses could therefore save significant amounts of water.

Evaporative water losses can be reduced by some 40–50% when the flue gas is cooled from around 140°C to 90–100°C before it enters the wet scrubber. This is commonly carried out in Japan and Europe using regenerative heat exchangers, but is less common in countries such as the USA. Additional benefits from cooling the flue gas include smaller flue gas volumes to be treated, and hence smaller FGD systems and stack requirements for new plants, and improved performance of existing ESPs and fabric filters. Moreover, mercury capture increases, and installing the heat exchangers upstream of the particulate control device can reduce SO_3 emissions to below 0.1 ppm through condensation on the fly ash. But regenerative heat exchangers are expensive, and can have high operating and maintenance costs. Power consumption increases, and leakage of the unscrubbed gas into the scrubbed gas decreases SO_2 removal efficiency. Non-leakage heat exchangers are commercially available.

Recovering 20% of the water in the flue gas would enable a power plant to become self-sufficient, but if over 20% is captured, then the plant would become a water supplier instead of a consumer. In addition, producing a low temperature flue gas with reduced acid and water vapour contents would lower the cost of capturing CO_2 in amine and ammonia scrubbers. Installing condensing heat exchangers can recover both heat and water from the flue gas. The recovered heat could be used in the boiler or turbine cycle to improve boiler efficiency. Water capture efficiency is limited to around 20% when cold boiler feedwater is the cooling fluid, but reaches some 70% with an inlet cooling water temperature of 24°C. It can be further enhanced through a combination of water- and air-cooled heat exchangers. Condensing the flue gas to recover the water requires a large cooling capacity, can lead to corrosion and fouling of the heat exchanger, and increases auxiliary power consumption. The recovered water has to be treated before it can be recycled, and this can be costly. Water condensation is more efficient with high moisture coals and at lower flue gas temperatures, and therefore may not be a practical option for low moisture coals.

Membranes that are highly selective for water vapour can recover at least 40%, and up to 90%, of the water vapour in the flue gas exiting the wet scrubber. A membrane condenser system also recovers the latent heat in the flue gas. The recovered water is mineral-free and can be utilised directly within the power plant, by industry or for public consumption purposes. No wastewater is produced. Parasitic

power consumption is around 0.1-1.1%. An economic analysis has shown that membrane systems produce demineralised water at a lower cost than a conventional demineralisation plant sited in the Netherlands. Combining the water capture membranes with CO₂-selective membranes could lower CO₂ emissions at the same time.

Pilot-scale tests have shown that a liquid desiccant-based dehydration system can recover 50–70% of the water vapour in the flue gas exiting the wet scrubber. Low grade heating and cooling sources within the power plant could be utilised to minimise the power needs of the process. The recovered water can be employed for direct cycle make-up after minimal treatment or used directly for other power plant applications. The economic viability of the process strongly depends on the location of the plant. Corrosion could be an issue with salt-based desiccants, and questions remain as to the long-term interaction of the desiccant with the flue gas, contamination of the desiccant solution by flue gas constituents, and precipitates that may form and how to handle them.

The semi-dry scrubbing systems, namely spray dry scrubbers (SDSs) and circulating dry scrubbers (CDSs), consume about 60% less water than wet scrubbers. Furthermore, they have the advantages of lower investment costs (than a similar sized wet scrubber), no production of wastewater, dry by-products, lower parasitic power consumption, a smaller footprint (which may be easier for retrofit applications), and additionally capture over 95% of the SO₃, HCl, HF and oxidised mercury. The main drawback of SDSs compared to wet scrubbers is their lower SO₂ removal efficiency (90–97%). State-of-the-art CDSs can remove over 98%, approaching the efficiency of wet scrubbers. Operating costs are generally higher than those for wet scrubbers mainly due to the higher sorbent costs, and maintenance costs of fabric filters in CDS systems can be higher due to their greater wear from the recycling of by-products. Multiple absorber vessels are required for units with a capacity higher than about 400 MW.

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 water usage, power consumption and capital costs. CDS systems consume some 20% more reagents than SDSs. Although CO_2 is not generated in the desulphurisation process, it is emitted from the on-site lime kilns (if present).

Sorbent injection processes have the lowest water consumption of the various FGD systems, consuming no water, or a minimal amount if the sorbent needs hydrating or the flue gas is humidified to improve performance. They are simple to install and operate, easy to retrofit with their small space requirements, and produce no wastewater. A co-benefit is the capture of some of the HCl, HF and mercury in the flue gas. The by-products are dry and so are easier to handle and manage than the wet by-products from wet scrubbers. As a consequence, the capital cost and energy consumption of the sorbent injection systems are considerably lower than the semi-dry and wet FGD processes. Parasitic power consumption is around 0.2% of electric capacity. Nevertheless, operating cost is the price of the sorbent. In general, calcium-based sorbents are cheaper than the sodium-based ones. The sorbent injection systems are best suited for use in small (<300 MWe) power plants that utilise low to medium sulphur coals, and where only a moderate SO₂ removal efficiency is required.

The main drawback of injection systems is the poor utilisation and SO_2 removal efficiency of the sorbents. The SO_2 (and SO_3) removal rate is dependent on a number of factors, including the injection location, flue gas temperature, sorbent particle size and reactivity, residence time, and the type of particulate control device. A power plant with fabric filters installed downstream of the injection point generally achieves a higher (~5–10%) SOx removal efficiency than one with ESPs, as the filter cake on the fabric filter provides additional time and contact for the SO_2/SO_3 to react with the sorbent. Injecting calcium-based sorbents either into the furnace or duct removes up to 60% of the SO_2 . The efficiency can be increased by around 10% with flue gas humidification. Injecting the sorbent as a slurry, with additives or recycling the sorbent after reactivation can also improve the utilisation and

 SO_2 removal efficiency. Sodium-based sorbents have a higher efficiency, capturing up to 90% of the SO_2 when injected into the duct, without the need for flue gas humidification. Sodium-based sorbents, though, cannot be used to capture SO_2 within the furnace. Injecting calcium-based sorbents decreases the efficiency of ESPs due to the increase in ash resistivity, requiring additional measures to mitigate this effect. On the other hand, sodium compounds may improve ESP performance due to the increase in ash resistivity. A disadvantage with the injection of carbonate-based sorbents (such as limestone, sodium carbonate and trona) is the formation of CO_2 , thus adding to the plant's CO_2 emissions. The by-products from the sorbent injection have little economic value.

When present in sufficient quantity, SO_3 (via the formation of H_2SO_4) can lead to stack opacity problems, increase corrosion and fouling of ductwork and equipment downstream of the furnace, decreasing their efficiency and penalising overall plant heat rate. SO_3 formation increases when an SCR is installed to control NOx emissions. Injecting calcium hydroxide and sodium-based sorbents into the ductwork downstream of the SCR can reduce SO_3 emissions more efficiently than wet scrubbers. A higher SO_3 removal efficiency is achieved with sodium-based sorbents, up to 98% in some cases. Trona, though, is more difficult to handle than hydrated lime due to its small particle size (~28 µm), its cohesiveness, and affinity for moisture. In addition, care must be taken to avoid the formation of liquid sodium bisulphate which can foul the downstream equipment and ductwork.

A concern with sorbent injection and semi-dry scrubbing processes is the effect of the collected spent sorbent on the saleability of the fly ash. A particulate collection device prior to the FGD unit may enable the fly ash to be sold, as well as the desulphurisation products. Calcium sulphate, for instance, could be sold as a fertiliser. Pre-collection of fly ash is widely practised in Europe but is not as common in the USA. The spent sorbent/fly ash mixtures from the processes have little marketable value, unlike the gypsum by-product from limestone wet scrubbers. More research on ways to utilise the by-products is required. Moreover, there is a need to develop effective reagents that can remove SOx at a lower sorbent:sulphur molar ratio, and hence generate less by-products. The development of sorbents with a higher reactivity for sulphur that could be used dry, and without the need for flue gas humidification, could lower water usage.

Multi-pollutant processes that remove several regulated pollutants in one system may be more costeffective than separate components. The commercial ReACTTM process is a regenerable system that uses only 1% of the water required by conventional wet scrubbers. Over 99% of SO₂ and SO₃, 20–80% NOx, >90% of mercury (both elemental and oxidised) and around 50% of the particulates are removed in the process when burning low to medium sulphur coals. Parasitic power consumption is about 0.7%. Saleable by-products are produced (the fly ash is pre-collected), and the mercury can be recovered from the spent activated coke off-site. Operating costs could be reduced if cheaper and more efficient activated carbon sorbents were developed.

The commercial SNOXTM is a regenerable catalytic process that consumes no water and removes up to 99% of SO₂ and SO₃, up to 96% of NOx and essentially all of the particulates. It produces saleable sulphuric acid and fly ash (since the ash is pre-collected), and no waste products, except for very low quantities of catalyst degradation fines. There is no parasitic power consumption because of the heat recovery features and, on a 500 MW power plant, a potential net power gain. SNOXTM has lower capital, operating, and maintenance costs than a wet limestone FGD + SCR plant burning high sulphur coals, but will cost more than a wet scrubber when combusting low and medium sulphur coals. The process was designed for high sulphur fuels.

The desulphurisation component of the two newer technologies, Cansolv® and CEFCO, can be installed separately if just FGD is required. The Cansolv® SO₂ system can be integrated with a CO₂ capture module to remove about 90% of the CO₂, whilst the CEFCO sulphur reactor system can be combined with modules removing over 99.9% of the trace metals (including mercury), fine particulates and NOx, and around 90% of CO₂. The sulphur modules are among the most efficient SO₂ removal processes available with both technologies removing over 99.9% of SO₂.

Conclusions

A separate SO₃ removal system may be required with the Cansolv® SO₂ scrubbing system in order to meet strict SO₃ emission regulations since only some 50% of SO₃ is captured by the proprietary amine solvent. Water consumption is relatively low, primarily because of the regeneration of the amine/water solvent and the recovery of water from the SO₂-rich gas. Furthermore, heat recovery reduces both the amount of steam necessary to regenerate the solvent and the amount of cooling water needed to cool the solvent. Energy consumption is relatively low, the footprint is smaller than a wet FGD system, and a saleable by-product can be produced from the recovered SO₂. The pre-collected fly ash can be sold.

The CEFCO process, currently at the pilot stage, captures over 99.9% of both SO₂ and SO₃. It is a net generator of water, saleable fertilisers can be produced and the fly ash sold (since it is pre-collected). Parasitic power consumption for the sulphur reactor module is around 3% when firing subbituminous and bituminous coals, and nearly 6% with lignite. The energy penalty (~23%) could be excessive in lignite power plants for the full four module multi-pollutant system.

To conclude, there are a number of commercial low water FGD processes available that are suitable for coal-fired power plants in areas where water is scarce. These technologies are either completely dry or have a relatively low water usage. Moreover, recovery of the water vapour in the flue gas exiting conventional wet scrubbers could enable a power plant to become a net supplier of water. Furthermore, technologies that produce a low temperature flue gas with low SOx and water vapour contents could lower CO_2 scrubbing costs, if future regulations require the installation of CO_2 control systems.

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