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Towards clean energy production

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Abstract

Implementation of stringent regulations of emission from power plants requires the development of new strategies and technologies for removal of pollutants from exhaust gases. This article summarizes current state of PM, NO_x, SO₂ and CO₂ abatement methods. The review is focused on the methods proved in industrial practice at commercially available and pilot installations.

Keywords: Emission control; Exhaust; Nitrogen oxides; Sulfur oxides; Carbon dioxide

1 Introduction

Nowadays the term *clean energy* most people associate with renewable energy, especially wind, solar, hydroelectric and geothermal. This is because none of those energy sources use fossil fuels neither emit carbon dioxide. As for carbon dioxide (CO₂) also biomass is considered a renewable energy source since CO₂ mass consumed in the life cycle by living organisms composing biomass is equal to CO₂ mass emitted during biomass/biogas combustion. Apart from gaseous pollutants an emission of particulate matter (PM) is also of great interest, and not only from coal fired boilers but also from biomass combusting installations.

In spite of all efforts of European Commission and some other countries

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towards dissemination of energy production from renewable sources still fossil fuels will play an important role even in developed countries for the next few decades. For that reason researchers all over the world do not stop activities in finding new ways to improve flue gases quality.

Reducing fuel combustion via an efficient and rational use of energy (energy management) may be therefore an efficient measure to reduce emissions of all pollutants and of greenhouse gases. Energy management may also contribute to increasing security of energy supply and a reduced consumption of natural resources. On the level of stationary installations but also on the level of production sites energy management means to increase overall energy efficiency by a number of different measures which can be realized alone or at best in combination like:

- implementation of an energy efficiency management system (ENEMS),
- establishment of a systems view for energy efficiency,
- benchmarking,
- energy efficient design (EED),
- process integration,
- expertise and know-how gains on energy efficiency,
- effective control, maintenance and monitoring of installations.

The best available technique (BAT) is the optimization of the combustion and steam systems but also the systems for compressed air, pumping, heating, cooling, ventilation, lighting, and other physical and chemical processes using a large number of techniques. Of particular importance are also heat recovery and cogeneration if reasonable.

Besides energy management which focuses more on the demand side, the supply side for energy has also a large impact on air emissions. Besides fuel switch where one (fossil) fuel is replaced by another also a change in the energy mix should be considered taking into account country specific conditions such as infrastructure, energy policy and availability of resources of fossil fuels and renewable energy like wind power, solar energy, geothermal energy or biomass. Burning more biomass, especially in stoves, may, however, also lead to increasing air emissions.

Unfortunately, energy management does not satisfy regulations on flue gas purity. Thus, other measures of pollutants emission must be applied. In this short review only main aspects concerning emission of particulate

matter (PM), nitrogen oxides (NO_x), sulfur oxides (SO_x) and carbon dioxide (CO_2) are presented. Much more can be found in thematic review papers [1–7].

2 Flue gas dedusting

Dust refers to a complex mixture of small to tiny particles and liquid droplets suspended in air. Sizes of dust range from several nanometers up to $100\text{ }\mu\text{m}$. Dust may be differentiated according to the aerodynamic diameter into:

- large particles with an aerodynamic diameter of more than $10\text{ }\mu\text{m}$,
- coarse particles with an aerodynamic diameter of 2.5 to $10\text{ }\mu\text{m}$,
- fine particles with an aerodynamic diameter of less than $2.5\text{ }\mu\text{m}$,
- ultrafine particles with an aerodynamic diameter of less than $0.1\text{ }\mu\text{m}$,

and more particularly into:

- total suspended particles (TSP) as the sum of fine, coarse and large particles;
- PM₁₀: the mass of particulate matter that is measured after passing through a size-selective inlet with a 50% efficiency cut-off at $10\text{ }\mu\text{m}$ aerodynamic diameter;
- PM_{2.5}: the mass of particulate matter that is measured after passing through a size-selective inlet with a 50% efficiency cut-off at $2.5\text{ }\mu\text{m}$ aerodynamic diameter;
- PM₁: the mass of particulate matter that is measured after passing through a size-selective inlet with a 50% efficiency cut-off at $1\text{ }\mu\text{m}$ aerodynamic diameter.

In order to reduce dust formation and dust emissions different types of measures like energy efficiency improvements, fuel switching, fuel cleaning, better handling of materials as well as abatement measures are applied.

2.1 Fuel switching

Fuel switching is an important option to reduce dust emissions from combustion but is governed by country specific conditions such as infrastructure

and energy policy. Dust emissions are in general lower if the fuel allows a more homogenous combustion, contains less sulfur and less ash but more hydrogen. Therefore, combustion of natural gas is in general associated with low emissions whereas high dust emissions result from combustion of fuel oil, biomass and coal if no abatement measures are applied.

The choice of the fuel may also have effects on other emissions like sulfur, NO_x and greenhouse gas emissions as well as on applicability and need of abatement measures.

2.2 Fuel cleaning

Fuel cleaning is important for coal and fuel oil. Conventional coal cleaning techniques rely on gravity-based separation of ash and sulfur compounds using jigs, dense-medium baths, cyclones or flotation of grinded coal. While 60% to 90% and 85% to 98% of the heating value of the coal is retained, ash removal can reach 60% and total sulfur removal 10% to 40%. Both sulfur and ash removal contributes to a reduction of dust emissions. Sulfur removal increases with the content of pyritic sulfur in the coal. Advanced techniques are mostly based on:

- advanced physical cleaning (advanced froth floatation; electrostatic, heavy liquid cycloning);
- aqueous phase pre-treatment (bioprocessing, hydrothermal, ion exchange);
- selective agglomeration (Otisca, LICADO, spherical agglomeration Aglofloat);
- organic phase pretreatment (depolymerization, alkylation, solvent swelling, catalyst addition (e.g., carbonyl), organic sulfur removal).

These advanced coal cleaning techniques are still in development or demonstration phase. Besides a reduction of sulfur and dust emissions, reported advantages are lower transportation costs if coal is cleaned already at the mine, higher boiler availability, less boiler slagging and fouling, less wear on equipment, lower dust load. Disadvantages are energy loss from cleaning (2–15%), energy costs for the processes and an increased moisture content of the coal if water-based processes are used.

2.3 Flue gas cleaning

The following secondary measures are mainly in use, each with its specific advantages and disadvantages according to the size of particles:

Cyclone In cyclones inertia of particles are used for dust removal. In a cyclone the flue gas is forced (usually via a conical shaped chamber) into a circular motion where particles are forced by inertia to the cyclone walls where they are collected. Collection efficiency depends strongly on particle size and increases with the pollutant loading. For conventional single cyclones it is estimated to be 70–90% for TSP (total suspended particulate), 30–90% for PM₁₀ and 0–40% for PM_{2.5} [6]. The minimum particle size removed by cyclones is 5–25 μm and 5 μm in multicyclones. Conventional cyclones are therefore referred to as ‘pre-cleaners’. Conventional cyclones alone are not the BAT for industrial installations but could be an option to reduce dust emissions from small combustion installations, e.g., in households or in the commercial sector. High efficiency cyclones removing 60–95% of PM₁₀ and 20–70% of PM_{2.5} have been developed but at the expense of a high pressure drop leading to high energy and hence operation costs. Achieving higher removal efficiencies in cyclones is mainly a problem of the resulting pressure drop. High throughput cyclones have been designed on purpose for removing just the larger dust fraction at the expense of only low pressure drop. In multicyclones many small cyclones operate in parallel achieving removal efficiencies similar or superior to high efficiency cyclones. Application of cyclones as a pre-cleaner to remove abrasive particles may increase the lifetime of other abatement equipment. Cyclones are also used to recover recycling products, process materials etc. from the flue gas, e.g., in the ferrous and nonferrous metals industry. Advantages of cyclones are: low investments, low operating and maintenance costs relative to the amount of PM removed, temperature and pressure range only limited by material, collection of dry material, relatively small in size. Disadvantages include low removal efficiencies for fine PM (or alternatively high pressure drops) and inapplicability for sticky materials.

Electrostatic precipitator The principle behind electrostatic precipitator (ESP) is that particles of the flue gas stream are electrostatically charged when passing through a region with gaseous ions (corona) generated by electrodes at high voltage (around 20 to 100 kV). The charged particles are then redirected in an electric field and settle at the collector walls. As large particles absorb more ions than smaller ones, ESP removal

efficiency is higher for larger particles. New ESP typically may achieve PM removal efficiencies of 99% to about 99.99% if perfectly dimensioned and in optimal operation conditions, in the range $0.01\ \mu\text{m}$ to $>100\ \mu\text{m}$, older ones 90% to 99.9% [8,5]. The minimum particle size removed by ESP is $<1\ \mu\text{m}$. Removal efficiencies are lowest for particles with a diameter of $0.1\ \mu\text{m}$ to $1\ \mu\text{m}$. Efficiency depends on the ESP size (collection area) but also on dust resistivity, temperature, chemical composition of the dust and gas and particle size distribution. The electrical conductivity of dust is one of the most relevant properties for ESP operation. In good and steady combustion conditions, particles are mainly composed of inorganic compounds such as salts which present ideal conductivity and are removed efficiently with the ESP. Soot and black carbon (BC) reveal high conductivity thus enabling high precipitation efficiency but severe re-entrainment of agglomerated particles. Condensable organic compounds (COC) from wood combustion (which are formed at low temperature from wood pyrolysis with characteristic compounds depending on residence time, heating rate, temperature and other operation parameters and at moderate temperatures and local lack of oxygen) exhibit low conductivity thus leading to back-corona which limits ESP operation [9]. Dust at the collectors can be removed either dry or wet by a spray of usually water (dry or wet ESP). Dry ESPs are more common as dry collected dust is easier to handle than slurry which requires after treatment. Wet ESPs need noncorrosive materials. However, removal of particles with extremely low or high resistivity is difficult in dry ESPs whereas wet ESPs can also collect particles with high resistivity as well as sticky particles, mists or explosive dusts. Wet ESPs show also higher efficiencies for smaller particles. Injection of conditioning gases, liquids or solids, in particular water and SO_3 , may improve removal efficiencies. Advantages of ESPs are in general very low pressure drops, very good removal efficiencies (but less pronounced for fine particles), low operating costs as well as wide applicability (sticky, glowing, high resistivity (wet ESP) particles, mists, acids, ammonia, exploding gases (wet ESP)). Disadvantages are high investments, high space demand, ozone formation due to high voltage, need for specialized personnel for high voltage, and limited applicability in case of varying flue gas conditions (flow rate, temperature, dust load, composition of dust) as well as necessary after treatment of slurry (wet ESPs), but almost closed water loops are achievable [8]. The lower efficiency of ESPs on submicrometer particles can be addressed by the use of an association of an ESP and a FF or the use of an agglomerator [5].

Fabric filter In a fabric filter (FF) the flue gasses pass through a permeable fabric where larger particles are sieved or adsorbed. The filter cake made up of collected particles supports the collection of further particles. As pressure drop increases with filter cake thickness the fabric filter needs to be cleaned from time to time. Three main cleaning mechanisms are applied: pulse jet filters where filters are cleaned by a pulse of pressurized air from the other side, shaker mechanisms and reverse gas flow. Pulse jet filters are today the most common type as they demand less space, are less expensive and applicable for high dust loadings and cause constant pressure drop. Removal efficiencies are 99% to 99.99% for new and 95 to 99.9% for older installations [8] and depend on filtration velocity, particle and fabrics characteristics and applied cleaning mechanism. FF is in particular able to remove fine and ultrafine dust. New developments are the addition of activated carbon or lime to achieve reactions in the filter cake as well as a catalytic filter material. Flue gas temperature depends on the filter material used and the dew point of the flue gas and is in general between 120–180 °C. Advantages of FF are very low emission levels even down to ultrafine particles (depending on fabric) and achieved independent from dust loading, flow rate (e.g., start-ups) and dust type (except tars due to their sticky properties [9]), simple operation and in general no corrosion problems. Disadvantages are relatively high maintenance and operating costs due to replacement of filter bags (lifetime depends on temperature and dust) and pressure drop and in particular limitations in applicability in moist environments and for hygroscopic, glowing and sticky particles as well as for acids and ammonia and exploding gases [8].

Wet scrubber Injecting water into the flue gas stream leads to formation of water droplets which with dust, forms a slurry. Scrubbers are mainly used for SO_x removal but reduce also dust. Removal efficiencies are up to 80% for spray towers as well as dynamic and collision scrubbers and up to 99% for Venturi scrubbers [8]. The minimum particle size removed by spray towers is $>10 \mu\text{m}$, by dynamic and collision scrubbers $>2.5 \mu\text{m}$ and by Venturi scrubbers $>0.5 \mu\text{m}$. Advantages of wet scrubbers are simultaneous removal of SO_x and dust – and even other pollutants like hydrogen chloride (HCl) and hydrogen fluoride (HF) – low maintenance, rather high removal efficiencies (in particular venturi scrubbers), few application limits (flow rate fluctuations, hot or cold, wet and corrosive gases, mists are uncritical) and reduced explosion risks from dust. Disadvantages are waste

generation (slurry), high maintenance costs due to potentially high pressure drop, corrosion problems and rather low removal efficiency for very fine particles such as those to which BC is associated [8].

To sum up, a variety of measures to reduce dust emissions exist. Some like cyclones are able to reduce the large and to some extent also the coarse fraction but are considerably less efficient for the fine fraction of dust. For fine and submicron dust fabric filters achieve very high removal efficiencies (up to 99.99% and above). Highly efficient ESPs, in particular Wet ESPs, as well as Venturi scrubbers may also achieve relatively high removal efficiencies for this size class up to 95% to 99%. Emerging hybrid techniques like agglomeration might contribute to increase ESP efficiency for fine particles by increasing the particle size [5]. An overview of precipitation efficiencies as function of the particle size for available technologies is presented in Fig. 1.

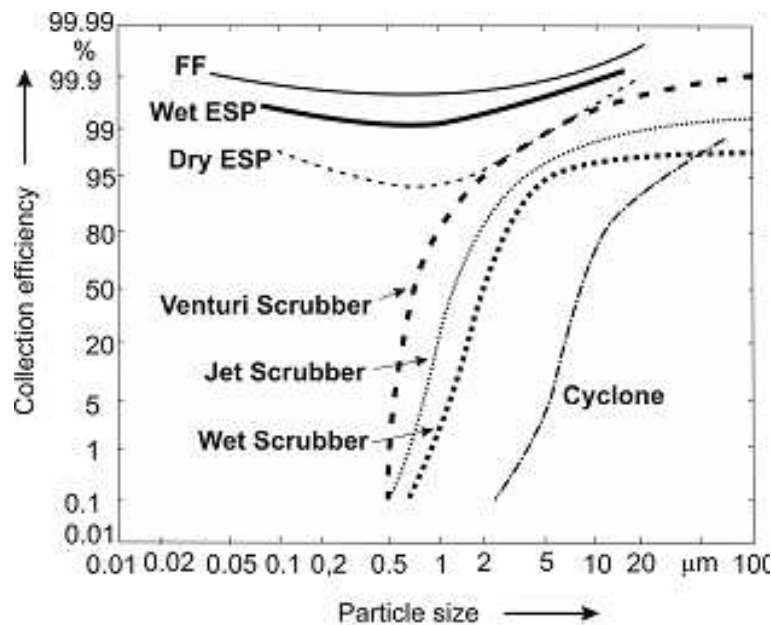


Figure 1: Precipitation efficiency for different gas cleaning systems (adapted from [9]).

However, when comparing removal efficiencies it need to be taken into account the characteristics of the dust and the flue gas as well as other parameters like dust load, flow rate, fluctuations as these factors may have a large impact on overall and size-specific removal performance. Furthermore re-

removal rates largely depend on the specific design of the dust collector, e.g., on chosen filter material and ESP dimensioning, and in the end investment and operating costs.

2.4 Side effects

For ESPs a main side effect is electricity consumption for producing the corona and the electric field. However, as pressure drop is low in ESPs, overall electricity consumption is considerably lower than in FF where high pressure drops have to be compensated for. In wet ESPs treatment of the slurry is necessary but water recirculation reaches almost 100% so that waste consumption is low. As ESPs have considerably lower removal efficiencies in the size range $0.1\ \mu\text{m}$ to $1\ \mu\text{m}$ removal of heavy metals in ESPs is far lower than in FF.

As for fabric filters, they have to be changed around every 2 to 4 years (lifetime depends on various factors) so that waste is generated if reprocessing of the fabrics is not possible. The pressure drop in FFs has to be compensated for by pumping leading to additional electricity consumption. As FFs are also very effective in removal of fine particles, they also effectively reduce emissions of heavy metals which are enriched in the submicrometer size range of dust in flue gases.

3 Limiting NO_x emission

The generic term NO_x refers to the sum of nitrogen oxide (NO) and nitrogen dioxide, expressed as NO_2 . The main source for NO_x is combustion where primarily NO is formed. NO is then rapidly converted to NO_2 .

In combustion, three main types of NO_x formation are distinguished:

- **Thermal NO_x** Molecular nitrogen (N_2) from air and molecular oxygen (O_2) dissociate at high temperature and react to form NO_x . The reaction is reversible and usually becomes significant at temperatures above around 1300°C . NO_x formation increases with temperature and residence time;
- **Fuel NO_x** In fuel NO_x , the nitrogen source for NO_x formation is the fuel itself. Two path ways may be distinguished: i) during initial combustion, volatiles including oxidized nitrogen are released and ii) during later stages when the char is oxidized and the nitrogen contained in the char is oxidized to NO_x . Fuel NO_x formation is

significant at temperatures above about 800 °C. The amount of fuel NO_x depends on the N content of fuels and on combustion conditions;

- **Prompt NO_x** Fuel radicals react with molecular nitrogen (N_2) from the air to form NO_x . Compared to thermal and fuel NO_x , prompt NO_x is of lesser importance for the sources considered here.

To achieve the most efficient NO_x reduction a combination of energy management and other measures should be considered. Other measures means pre-combustion, combustion and post-combustion methods. To identify the best combination of measures, a site-specific evaluation is needed.

3.1 Pre-combustion and combustion modification

The aim of pre-combustion methods is reducing the amount of nitrogen in the fuel. Switching to low NO_x producing fuels is one option to reduce NO_x emissions but is governed by country specific conditions such as infrastructure and energy policy. Fuels with high nitrogen content like heavy fuel oil and coal may lead to high fuel NO_x formation and hydrogen rich fuels like natural gas as a result of high combustion temperatures to high thermal NO_x formation [10]. The choice of the fuel may also have effects on other emissions like sulfur, particulate matter and greenhouse gas emissions as well as on applicability and need of abatement measures.

Combustion modification is aimed at forming oxygen deficient stoichiometric conditions, reducing flame temperature or changing the residence time within different parts of the combustion zone in order to reduce NO_x formation and increase reconversion of NO_x to N_2 and O_2 [11,12].

- **Reducing peak temperature** As thermal NO_x formation depends largely on the combustion temperature, a reduction in temperature is one option to reduce NO_x formation. Reducing peak temperature can be achieved by the following methods: i) diluting the heat produced during the combustion process, ii) cooling down, and iii) reducing the oxygen available for combustion but also by applying other combustion techniques like fluidized bed combustion (FBC) which operates at lower temperatures and includes an inherent air-staging. Main methods for reducing peak temperature are:
 - substoichiometric combustion, i.e., using a fuel-rich mixture so that oxygen is a limiting factor (fuel acts also as reducing agent),
 - suprastoichiometric combustion, i.e., using a fuel-lean mixture to dilute combustion heat;

- injecting cooled oxygen-depleted fuel gas to dilute combustion heat;
 - injecting cooled oxygen-depleted fuel gas with added fuel to dilute combustion heat, to reduce the reaction temperature and to make oxygen a limiting factor;
 - injecting water or steam to dilute combustion heat and to reduce the reaction temperature.
- **Reducing residence time at peak temperature** As thermal NO_x formation depends largely on the time the fuel gas remains in the high temperature region, reducing this residence time reduces also NO_x formation. Methods to reduce residence time include:
 - injection of fuel, steam, recirculated flue gas or combustion air immediately after combustion,
 - reducing the extension of the high temperature zone which can be faster left by the flue gas then.
 - **Chemical reduction of NO_x during combustion process** NO_x can be reduced to N_2 using a reducing agent which is itself oxidized. The principle of chemical reduction is widely used in secondary measures but can be also used as a primary measure when reduction takes already place during the combustion process. Main methods are:
 - substoichiometric combustion, i.e., in a fuel rich mixture so that the remaining fuel may act as reducing agent;
 - reburning of the flue gas with fuel added (with the added fuel acting as a reducing agent);
 - generation of fuel-lean and fuel-rich conditions in the combustion zone.

The following technologies which are based on the principles and methods described above are mainly in use, each with its specific advantages and disadvantage. Some of the technologies are typical for retrofit, others for new installations and others are only applicable in new installations [2]:

- Low excess air (LEA) – reducing oxygen availability; this can be easily applied to existing power plants, however may result in high level of CO (incomplete burning) and reduction of NO_x is low (10–44%).

- Air staging (AS) – the principle of air staging is to create two zones, one fuel-rich zone where initial combustion takes place and a second one where air is added to ensure complete combustion. This allows reducing thermal NO_x formation in the first zone where less nitrogen is available and in the second where temperature is lower. The zone may be created in different ways. In biased burner firing (BBF) air and fuel flow rates are varied, in Burners Out of Service (BOOS) the fuel flow to the burner is cut for a short time and in overfire air (OFA) air is injected above the normal combustion zone. Staged air combustion is frequently used in conjunction with low NO_x burners (LNB).
- Fuel staging (FS) – fuel staging is similar to air staging but with fuel instead of air. The first stage is extremely fuel-lean which reduces the temperature. Fuel added in the second stage acts as a reducing agent for formed NO_x . In a third stage air is added to ensure burnout.
- Low NO_x burners (LNB) – low NO_x burners mix fuel and air/flue gas in a way so that different zones are created as in staged combustion. The zoning allows lower flame temperature and oxygen concentration as well as chemical reduction of NO_x by fuel in some of the zones. Low NO_x burners can be further differentiated into air-staged LNB, flue-gas recirculation LNB and fuel-staged LNB depending on the principle used for reducing NO_x emissions. a further development is the ultra low NO_x burner. LNBs can reduce NO_x up to 60%.
- Flue gas recirculation (FGR) – recirculating cooled flue gas reduces the combustion temperature in a secondary combustion stage and also oxygen concentration so that thermal NO_x formation is reduced. Heat of the flue gas may be recovered in a heat exchanger. Recirculation up to 30% of flue gas with air can give up to 50% NO_x reduction.
- Water/steam injection – water and steam are injected to cool the flame and to reduce thermal NO_x formation. It results in NO_x reduction of 70–80%.
- Fuel reburning (FR) – fuel reburning is similar to flue gas recirculation but with added fuel in the flue gas leading to lower temperatures. If added in a second combustion stage fuel re-burning makes use of the fuel as reducing agent and is similar to fuel staging. This method can give 50–60% of NO_x reduction.

- Plasma assisted combustion (PAC) – using non-thermal plasma as a first-stage combustor; this can give up to 65% NO_x reduction [13].

Generally, efficiency of NO_x reduction by pre- and combustion methods depends on the type of the combustion system. It is possible to achieve 30–70% NO_x reduction and up to 70–85% for gas turbines [2].

3.2 Post-combustion methods

Post-combustion technologies have been extensively used and developed, since they can provide high NO_x emission reduction. However, nowadays it is difficult to fulfill the stringent emission requirements using just one strategy. Skalska *et al.* [2] prepared a very clear scheme that summarizes all the post-combustion methods (Fig. 2). Among them, physical methods are not preferable due to the main drawback which is the NO_x transfer from flue gas into another medium requiring further treatment. Presently, the only commercially available methods are selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) of NO_x. The aim of both technologies is to reduce NO_x in the flue gas to harmless N₂. Excellent review papers dealing with SNCR and SCR were elaborated by Cheng and Bi [12], and Javed *et al.* [14].

In SCR, NO_x is reduced to N₂ by a reducing agent (usually ammonia) which is directly injected into the flue gas over a catalyst in the presence of sufficient oxygen. NO_x-conversion takes place on the catalyst surface at a temperature between 170 °C and 510 °C (with a range between 300 °C and 400 °C being more typical, the minimum flue gas temperature is dependent on the sulfur content of the fuel. At a too low flue gas temperature ammonium bisulfate is formed which will clog the SCR elements. A limitation for the applicability of SCR exists for diesel engines which need to be operated in varying loads. These units are operated frequently on isolated systems to be operated for a reduced number of hours only. According to the electricity demand, these engines need to be started up and shut down several times a day. SCR is an applied technique for diesel engines, but cannot be seen as the BAT for engines with frequent load variation, including frequent start up and shut down periods due to technical constraints. A SCR unit would not function effectively when the operating conditions and the consequent catalyst temperature are fluctuating frequently outside the necessary effective temperature window.

In SNCR similar to SCR a reducing agent (usually ammonia, urea or

caustic ammonia) is used to reduce NO_x but in contrast to SCR, without a catalyst and at a higher temperature between 850°C and 1100°C .

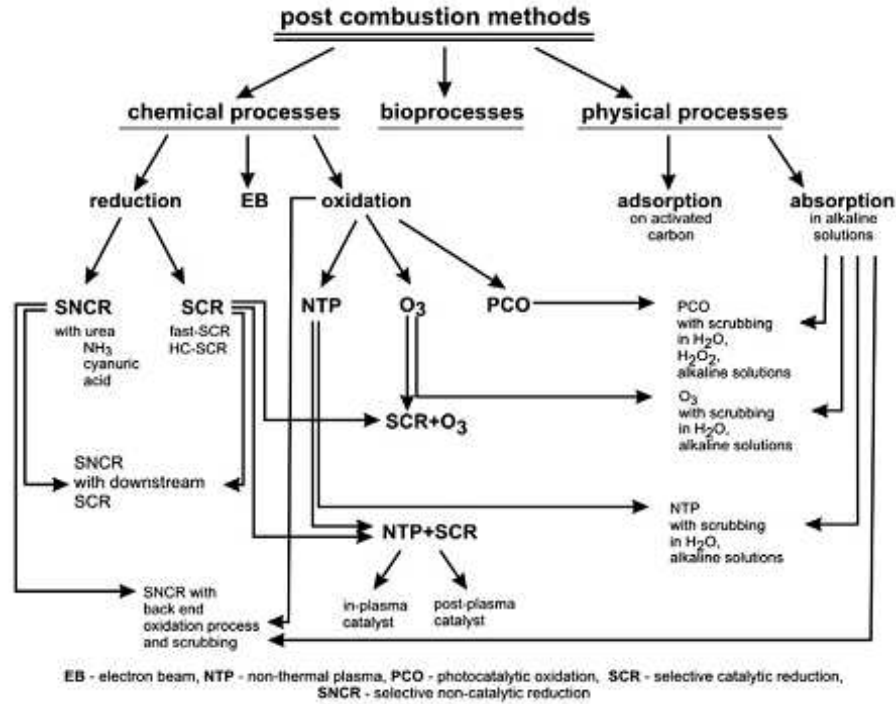


Figure 2: Schematic presentation of NO_x -reducing post-combustion methods. Reprinted from [2] with permission from Elsevier.

As for oxidation-based methods here only those tested in pilot plants are described. One of them is nonthermal plasma (NTP) generated by pulsed corona discharge or dielectric barrier discharge. Both reduction and oxidation of nitrogen oxides occur in such plasma. Reduction of NO into N_2 is driven by N radicals of different excitation state, whereas oxidation into NO_2 , HNO_2 and HNO_3 involves atomic oxygen, ozone and OH radicals formed from water vapor present in the flue gas. All active radicals are formed in the plasma due to collisions of energetic electrons with molecules. Industrial gas streams containing sulfur dioxide and nitrogen oxides generated by power plant have been treated under pulse discharge plasma in several pilot plants [15]. The last one was operational for several years in Korea [16]. An industrial power modulator integrating pulse induced plasma has been tested in decomposing simultaneously NO_x and SO_2 from

stream flow of 50 000 Nm³/h with a power supply of 120 kW and frequency of 240 Hz. NO_x and SO₂ removal rate was up to 70% and 99%, respectively. The particular removal rates are attributed to the incorporation of supplementary feed streams of propylene and ammonia.

Nonthermal plasma cannot achieve enough high NO_x removal from flue gases because of reverse reactions of acids and NO₂ into NO [16,17]. Because of that drawback it is combined with other techniques such as absorption process or solid catalysts. The first approach is a way of NO_x concentration in a liquid or solid medium which is then regenerated and concentrated NO_x are reduced. The second combination is the addition of a reducing agent to nonthermal plasma in the presence of a catalytic material. This is usually performed with the use of a catalyst. Practically, this is a better idea since it involves dry processes and the presence of 30% to 50% of NO_x in the form NO₂ in flue gas greatly enhances the performance of selective catalytic NO_x reduction [18]. The nonthermal plasma with a catalyst can be operated in two configurations: positioning the catalyst in the discharge zone (in-plasma catalysis) or downstream the discharge zone (post-plasma catalysis). More details can be found in two review papers by Van Durme *et al.* [18] and Telabizadeh *et al.* [19]. Unfortunately, due to a short lifetime of catalysts none of laboratory tested NTP reactors have been upscaled and tested with industrial flue gases.

Another promising NTP technology is electron beam flue gas treatment. This is a dry-scrubbing process of simultaneous SO₂ and NO_x removal, where no waste, except a by-product in the form of fertilizer, is generated [3]. The application of electron beam irradiation to initiate chemical reactions to remove SO₂ and NO_x was first investigated by joint research of the Japan Atomic Energy Research Institute (JAERI) and Ebara Corporation in the early 1980s. The method has been developed since then from the laboratory to pilot and a large demonstration scale by research and development projects in Japan, USA, Germany, China and Poland. Electron beam technology for coal-fired boilers has been implemented on an industrial scale at the thermal power plants (TPPs) at Chengdu and Hangzhou in China and at the power station Pomorzany in Poland. The plants in China were designed mainly for SO₂ removal, while the plant in Poland was designed for simultaneous SO₂ and NO_x removal. The flue gases from two Benson boilers (65 MW(e) and 100 MW(th) each) are purified at the EPS Pomorzany in Poland. The maximum flow rate of the gases is 270 000 Nm³/h and the total electron beam power is equal to 1 MW. There are two process vessels

over which two electron accelerators are installed in series (700 keV, 260 kW each). The applied radiation dose is in the range 7–12 kGy (kJ/kg). At these doses, the removal efficiency approaches 85–95% for SO₂ and 50–70% for NO_x. The by-product is collected by an electrostatic precipitator and shipped to a fertilizer plant. Electron beam technology has to be competitive with the conventional ones both from economic and technical point of view. Therefore, any development concerning cost reduction and technological improvements regarding technical components, especially reliability of electron accelerator plays a very important role for further electron beam technology implementation. Unfortunately, due to the economic reason, i.e., repair cost of accelerator, the last operational pilot station in Pomorzany was shut down recently.

3.3 Side effects

The side effects to be considered with different emission reduction techniques are:

- Pre-combustion methods: possible side effects are lower overall energy efficiency, increased CO and soot formation and hydrocarbon emissions, corrosion due to reducing atmosphere, increase in unburnt carbon in fly ash.
- FBC: this technique also brings about a considerable reduction in SO_x emissions. a possible drawback in FBC systems may be the increased formation of N₂O under certain process conditions. The handling of the ashes needs consideration in relation to their possible use and/or disposal.
- SCR: some possible side effects are ammonia slip in the exhaust gas, ammonia content in the fly ash, formation of ammonium salts on downstream facilities, deactivation of the catalyst and increased conversion of SO₂ to SO₃ (corrosion and fouling). By the controlled operation of the plant, the fly ash quality can, however, be guaranteed and the formation of ammonia salt reduced. In terms of by-products, deactivated catalysts from the SCR process may be the only relevant products, although this has become a minor problem since catalyst lifetime has been improved and reprocessing options exist. Biomass and waste burning can reduce catalyst life.
- SNCR: side effects to be considered are ammonia in the exhaust gas, formation of ammonium salts on downstream facilities, the formation

of N_2O , when urea, for instance, is used as a component of the reducing mixture, and CO releases. The ammonia slip from SNCR usually is much higher than from SCR due to the required over-stoichiometric dosage of the reducing agent (at the high temperatures required for SNCR, part of the injected ammonia reacts to form additional NO_x).

The production of ammonia and urea for flue gas treatment processes involves a number of separate steps which require energy and reactants. The storage systems for ammonia are subject to the relevant safety legislation and such systems are designed to operate as totally closed systems, with a resultant minimum of ammonia emissions. The use of NH_3 is still considered appropriate, even when taking into account the indirect emissions related to the production and transport of NH_3 .

4 Limiting SO_2 emission

The main techniques applied in order to reduce SO_x emissions from combustion processes are: energy efficiency improvement, fuel switching, fuel cleaning, combustion modification and post-combustion methods.

4.1 Pre-combustion methods

Similarly as in the case of NO_x emission control the aim of pre-combustion methods is reducing the amount of sulfur in the fuel either by fuel switching or fuel cleaning.

Fuel switching (e.g., from high- to low-sulfur coals and/or liquid fuels, or from coal or liquid fuel to gas) leads to lower sulfur emissions, but there may be certain restrictions, such as the availability of low-sulfur fuels and the adaptability of existing combustion systems to different fuels. In many EU countries, some coal or oil combustion plant is being replaced by gas-fired combustion plant. Dual-fuel plant may facilitate fuel switching. Fuel switching can also have beneficial effects on nitrogen dioxide or particulate matter emission levels.

Cleaning of natural gas is state-of-the-art and applied for operational reasons. Cleaning of process gas (acid refinery gas, coke oven gas, biogas, etc.) is also state-of-the-art technology. Desulfurization of liquid fuels (light and medium fractions) is state-of-the-art technology. Desulfurization of heavy fractions is technically feasible. Nevertheless, the crude oil properties should be kept in mind. Desulfurization of atmospheric residue

(bottom products from atmospheric crude distillation units) for the production of low-sulfur fuel oil is not, however, commonly practiced. Processing low-sulfur crude is usually preferable. Hydrocracking and full conversion technology has matured and combine high sulfur retention with improved yield of light products. The number of full conversion refineries is constantly rising. Such refineries typically recover 80% to 90% of the sulfur intake and convert all residues into light products or other marketable products. This type of refinery consumes more energy and requires higher investments. Sulfur content of refinery products needs to correspond to the restricted value ordered by the EU. Current technologies to clean hard coal can remove approximately 50% of the inorganic sulfur (depending on coal properties) but none of the organic sulfur. More effective technologies are being developed. However, they require higher specific investments. Thus the efficiency of sulfur removal by coal cleaning is limited compared to flue gas desulfurization. There may be a country-specific optimization potential for the best combination of fuel cleaning and flue gas cleaning.

4.2 Combustion modification

Advanced combustion may improve thermal efficiency and reduce sulfur emissions. These technologies include fluidized-bed combustion (FBC), integration gasification combined-cycle (IGCC), and combined-cycle gas turbines (CCGT). Stationary combustion turbines can be integrated into combustion systems in existing conventional power plant. This can increase overall efficiency by 5% to 7%, leading, for example, to a significant reduction in SO₂ emissions. However, major alterations to the existing furnace system become necessary. Reciprocating engines can also increase the electrical efficiency by taking advantage of the sensible heat of the exhaust gases generated by, e.g., use of a feed-water combined cycle.

In FBC, the combustion takes place through a particulate bed, which can be fixed (FFBC), pressurized (PFBC), circulating (CFBC) or bubbling (BFBC). Fluidized-bed combustion is a combustion technology for burning hard coal and brown coal, but it can also burn other solid fuels, such as petroleum coke, and low-grade fuels, such as waste, peat and wood. Emissions can be further reduced by integrated combustion control in the system due to the addition of lime/limestone to the bed material. The use and/or disposal of by-products from this process may cause problems and further development is required.

The IGCC process includes coal gasification and combined-cycle power

generation in a gas and steam turbine. The gasified coal is burnt in the combustion chamber of the gas turbine. Sulfur emission control is achieved by using state-of-the-art technology for raw gas cleaning facilities upstream of the gas turbine.

Combustion modifications comparable to the measures used for NO_x emission control do not exist, as during combustion the organically and/or inorganically bound sulfur is almost completely oxidized. A certain percentage, depending on the fuel properties and combustion technology, is retained in the ash. The amount of sulfur retained in ash, can be influenced by added sorbents (e.g., lime/limestone) and combustion conditions (e.g., temperature). Dry additive processes for conventional boilers may be considered as process modifications due to the injection of an agent into the combustion unit. However, experience has shown that, when applying these processes, thermal capacity is lowered, and the Ca/S ratio is relatively high and sulfur removal low. In recent years, the performance of these processes has nevertheless been optimized to the point that SO_2 removal efficiency reached 50–80%. Problems with the further use of the by-product have to be considered.

4.3 Post-combustion methods

These methods aim at removing already formed sulfur oxides from flue gases using wet, dry or semidry processes. Sulfur can also be removed using the recovery of sulfur dioxide from the flue gases and then extracted in a regenerative process. Flue gas scrubbing using water or seawater is another available technology to reduce SO_2 emissions.

In wet scrubbing technologies, the flue gas is first dedusted then cleaned by an atomized solution of alkaline compounds. SO_2 reacts with these alkaline compounds to form by products, whose chemical nature depends on the alkaline compound used. In the case of use CaCO_3 or CaO , by-products may be upgraded as gypsum if some technical conditions are achieved. By-products can also be upgraded using other scrubbing agent. With wet desulfurization, excellent efficiencies can be achieved ranging from 92% to 98% with a near-stoichiometry Ca/S ratio. This process is mainly used for reducing SO_2 emissions from coal power plants.

In the dry process, a calcium or sodium based sorbent is injected in solid form into the flue gases before a fabric filter or an ESP. Hydrated lime (Ca(OH)_2) or sodium bicarbonate (NaHCO_3) are the most frequently used sorbents. Sorbents need to be very reactive and are activated for this

purpose. They react with SO_2 to form calcium or sodium sulfites and sulfates, which need then to be filtered in order to reduce dust emissions. The dry duct injection process efficiency is lower than with wet desulfurization (about 50%) and depends on several parameters such as temperature, SO_2 content of the flue gas, Ca/S ratio and residence time.

Furnace sorbent injection is a direct injection of a dry sorbent in the gas stream of the boiler furnace. Pulverized limestone (CaCO_3) is used. Calcium sulfites and sulfates formed need to be captured by fabric filter or ESP. Efficiencies from 70 to 80 % may be obtained according to the arrangement used [20].

The semidry process or spray dry scrubbing is similar to the dry process and also produces a solid residue. It uses moisturized lime or limestone containing about 10% of water to enhance the contact and the reactions. The removal SO_2 efficiency ranges from 85% to 92% with a ratio Ca/S from 1.3 to 2 [21].

5 Limiting CO_2 emission

The main strategy of limiting CO_2 emission from fossil fueled power plants is carbon capture and storage (CSS). Generally CSS consists of 3 basic stages: separation, transport and storage [4]. The first and key step is separation from flue gas. It can be done by:

- absorption – the flue gas is cooled down to 318–323 K and then it flows to a scrubber where CO_2 is washed out using liquid solvent such as alkanolamines (monoethanolamine as the best) [22,23], carbonate-bicarbonate buffers, hindered amines, amino acids (glycine, alanine, dimethyl glycine, diethyl glycine, a number of sterically hindered amino acids) [24,25], piperazine [26], ammonia (to be withdrawn) [27];
- adsorption – catching CO_2 on the surface of porous materials operating as chemisorbents (CaO , MgO , metal salts from alkali metal compounds – especially lithium-based, hydrotalcites and double salts) [28] or physisorbents (activated carbon, zeolites, carbon nanotubes and many other porous materials) [29];
- cryogenic distillation – the components are separated by a series of compression, cooling, and expansion steps; the major disadvantage of this process is high operational costs due to the large amount of energy required for keeping low temperature [30,31].

New methods are also under development such as membrane separation, electrochemical separation and chemical looping, but due to many technical limitations they cannot be used at the moment for CO₂ capturing in energy producing installations.

Nowadays as well as in the near future absorption and adsorption processes are the BAT for CO₂ separation from flue gases. Although solvents require low energy for regeneration they have low absorption capacity and selectivity for CO₂ separation. That is why researchers are now focused on finding better solvents. On the other hand adsorption on porous materials is the effective technology that can reduce energy and cost of the CSS. However, so far they work efficiently only at high pressure (about 0.4 MPa) which is a problem for continuous CO₂ separation from a flue gas stream. For industrial application, more studies about adsorbents are necessary.

6 Summary

Most combustion installations use fuel and other raw materials taken from the earth's natural resources, converting them into useful energy. Fossil fuels are the most abundant energy source used today. Their combustion process leads to the generation of emissions mainly to air, of which emissions of NO_x, SO₂, CO₂ and PM are most important. Other substances such as heavy metals, halide compounds, and dioxins are emitted in smaller quantities. However, burning fossil fuels results in a relevant and, at times, significant impact on the environment as whole, i.e., water and soil is also affected. Below are summarized conclusions on clean energy production.

Particulate matter (dust) emitted during the combustion of solid or liquid fuels arises almost entirely from their mineral fraction. By combustion of liquid fuels, poor combustion conditions lead to the formation of soot. Combustion of natural gas is not a significant source of dust emissions. The emission levels of dust, in this case, are normally well below 5 mg/Nm³ without any additional technical measures being applied. For dedusting off-gases from new and existing combustion plants, BAT is considered to be the use of an electrostatic precipitator or a fabric filter, where a fabric filter normally achieves emission levels below 5 mg/Nm³. These technologies are also suitable for heavy metals removal. Cyclones and mechanical collectors alone are not BAT, but they can be used as a precleaning stage in the flue-gas path. It must be noticed that searching for new gas cleaning devices of higher collection efficiency for submicron particles became more important

in last decades because the regulations concerning this size range of particle become more stringent with each passing year.

Emissions of sulfur oxides mainly result from the presence of sulfur in the fuel. Natural gas is generally considered free from sulfur. In general, for solid and liquid-fuel-fired combustion plants, the use of low sulfur fuel and/or desulfurisation is considered to be BAT. However, the use of low sulfur fuel for plants over 100 MW_{th} can, in most cases, only be seen as a supplementary measure to reduce SO₂ emissions in combination with other measures. Besides the use of low sulfur fuel, the techniques that are considered to be BAT are mainly the wet scrubber (reduction rate 92–98%), and the spray dry scrubber desulfurisation (reduction rate 85–92 %), which already has a market share of more than 90%. Dry desulfurization techniques such as dry sorbent injection are used mainly for plants with a thermal capacity of less than 300 MW_{th}. The wet scrubber has the advantage of also reducing emissions of HCl, HF, dust and heavy metals. Because of the high costs, the wet scrubbing process is not considered as BAT for plants with a capacity of less than 100 MW_{th}.

For pulverized coal combustion plants, the reduction of NO_x emissions by primary and secondary measures, such as SCR, is BAT, where the reduction rate of the SCR system ranges between 80% and 95%. The use of SCR or SNCR has the disadvantage of a possible emission of unreacted ammonia ('ammonia slip'). For small solid fuel-fired plants without high load variations and with a stable fuel quality, the SNCR technique is also regarded as BAT in order to reduce NO_x emissions. For pulverized lignite and peat-fired combustion plants, the combination of different primary measures is considered as BAT. This means, for instance, the use of advanced low NO_x burners in combination with other primary measures such as flue-gas recirculation, staged combustion (air-staging), reburning, etc. The use of primary measures tends to cause incomplete combustion, resulting in a higher level of unburned carbon in the fly ash and some carbon monoxide emissions. In fluidized bed combustion boilers burning solid fuel, BAT is the reduction of NO_x emissions achieved by air distribution or by flue-gas recirculation. There is a small difference in the NO_x emissions from bubbling fluidized bed combustion and circulating fluidized bed combustion. For new gas turbines, dry low NO_x premix burners (DLN) are BAT. For existing gas turbines, water and steam injection or conversion to the DLN technique is BAT. For gas-fired stationary engine plants, the lean-burn approach is BAT analogous to the dry low NO_x technique used in gas turbines.

For most gas turbines and gas engines, SCR is also considered to be BAT. Retrofitting of an SCR system to a combined cycle gas turbine is technically feasible but is not economically justified for existing plants. There are also other techniques, such as those involving nonthermal plasma, which proved their usefulness for combined NO_x/SO_2 removal from flue gas but which still needs improvements before gaining commercial availability.

Besides the generation of air pollution, large combustion plants are also a significant source of water discharge (cooling and waste water) into rivers, lakes and the marine environment. Any surface run-off (rainwater) from the storage areas that washes fuel particles away should be collected and treated (settling out) before being discharged. Small amounts of oil contaminated (washing) water cannot be prevented from occurring occasionally at a power plant. Oil separation wells are BAT to avoid any environmental damage. The BAT conclusion for wet scrubbing desulfurisation is related to the application of a waste water treatment plant. The waste water treatment plant consists of different chemical treatments to remove heavy metals and to decrease the amount of solid matter from entering the water. The treatment plant includes an adjustment of the pH level, the precipitation of heavy metals and removal of the solid matter.

A lot of attention has already been paid by the sector to the utilization of combustion residues and by-products, instead of just depositing them in landfills. Utilization and reuse is, therefore, the best available option and has priority. There are many different utilization possibilities for different by-products such as ashes. Each different utilization option has different specific criteria. The quality criteria are usually connected to the structural properties of the residue and the content of harmful substances, such as the amount of unburned fuel or the solubility of heavy metals, etc. The end-product of the wet scrubbing technique is gypsum, which is a commercial product for the plant in most EU countries. It can be sold and used instead of natural gypsum. Practically most of the gypsum produced in power plants is utilized in the plasterboard industry. The purity of gypsum limits the amount of limestone that can be fed into the process.

It must be also pointed out that prudent management of natural resources and the efficient use of energy are two of the major requirements of the integrated pollution prevention and control (IPPC) directive of European Commission. In this sense cogeneration (CHP – combined heat and power) is considered as the most effective option to reduce the overall amount of CO_2 released and is relevant for any new build power plant

whenever the local heat demand is high enough to warrant the construction of the more expensive cogeneration plant instead of the simpler heat or electricity only plant.

The survey of strategies and technologies presented in this paper shows only main problems associated with clean energy production. It has not been possible to cover all environmental and scientific aspects. However, one may consider information compiled above as useful for educational purpose at least.

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