ANNEX IV

Control technologies for sulphur emissions from stationary sources

I. INTRODUCTION

1. The aim of this annex is to provide guidance for identifying sulphur control options and technologies for giving effect to the obligations of the present Protocol.

2. The annex is based on information on general options for the reduction of sulphur emissions and in particular on emission control technology performance and costs contained in official documentation of the Executive Body and its subsidiary bodies.

3. Unless otherwise indicated, the reduction measures listed are considered, on the basis of operational experience of several years in most cases, to be the most well-established and economically feasible best available technologies. However, the continuously expanding experience of low-emission measures and technologies at new plants as well as of the retrofilling of existing plants will necessitate regular review of this annex.

4. Although the annex lists a number of measures and technologies spanning a wide range of costs and efficiencies, it cannot be considered as an exhaustive statement of control options. Moreover, the choice of control measures and technologies for any particular case will depend on a number of factors, including current legislation and regulatory provisions and, in particular, control technology requirements, primary energy patterns, industrial infrastructure, economic circumstances and specific in-plant conditions.

5. The annex mainly addresses the control of oxidized sulphur emissions considered as the sum of sulphur dioxide (SO\textsubscript{2}) and sulphur trioxide (SO\textsubscript{3}), expressed as SO\textsubscript{2}. The share of sulphur emitted as either sulphur oxides or other sulphur compounds from non-combustion processes and other sources is small compared to sulphur emissions from combustion.

6. When measures or technologies are planned for sulphur sources emitting other components, in particular nitrogen oxides (NO\textsubscript{x}), particulates, heavy metals and volatile organic compounds (VOCs), it is worthwhile to consider them in conjunction with pollutant-specific control options in order to maximize the overall abatement effect and minimize the impact on the environment and, especially, to avoid the transfer of air pollution problems to other media (such as waste water and solid waste).

II. MAJOR STATIONARY SOURCES FOR SULPHUR EMISSIONS

7. Fossil fuel combustion processes are the main source of anthropogenic sulphur emissions from stationary sources. In addition, some non-combustion processes may contribute considerably to the...
emissions. The major stationary source categories, based on EMEP/CORINAIR 90, include:

(i) Public power, cogeneration and district heating plants:
   (a) Boilers;
   (b) Stationary combustion turbines and internal combustion engines;

(ii) Commercial, institutional and residential combustion plants:
   (a) Commercial boilers;
   (b) Domestic heaters;

(iii) Industrial combustion plants and processes with combustion:
   (a) Boilers and process heaters;
   (b) Processes, e.g. metallurgical operations such as roasting and sintering, coke oven plants, processing of titanium dioxide (TiO₂), etc.;
   (c) Pulp production;

(iv) Non-combustion processes, e.g. sulphuric acid production, specific organic synthesis processes, treatment of metallic surfaces;

(v) Extraction, processing and distribution of fossil fuels;

(vi) Waste treatment and disposal, e.g. thermal treatment of municipal and industrial waste.

8. Overall data (1990) for the ECE region indicate that about 88 per cent of total sulphur emissions originate from all combustion processes (20 per cent from industrial combustion), 5 per cent from production processes and 7 per cent from oil refineries. The power plant sector in many countries is the major single contributor to sulphur emissions. In some countries, the industrial sector (including refineries) is also an important SO₂ emitter. Although emissions from refineries in the ECE region are relatively small, their impact on sulphur emissions from other sources is large due to the sulphur in the oil products. Typically 60 per cent of the sulphur intake present in the crudes remains in the products, 30 per cent is recovered as elemental sulphur and 10 per cent is emitted from refinery stacks.

Up to the Table of Contents}

III. GENERAL OPTIONS FOR REDUCTION OF SULPHUR EMISSIONS FROM COMBUSTION

9. General options for reduction of sulphur emissions are:

(i) Energy management measures:

   (a) Energy saving
   The rational use of energy (improved energy efficiency/process operation, cogeneration and/or demand-side management) usually results in a reduction in sulphur emissions.

   (b) Energy mix
In general, sulphur emissions can be reduced by increasing the proportion of non-combustion energy sources (i.e. hydro, nuclear, wind, etc.) to the energy mix. However, further environmental impacts have to be considered.

(ii) Technological options:

(a) Fuel switching

The SO\textsubscript{2} emissions during combustion are directly related to the sulphur content of the fuel used. Fuel switching (e.g. from high- to low-sulphur coals and/or liquid fuels, or from coal to gas) leads to lower sulphur emissions, but there may be certain restrictions, such as the availability of low-sulphur fuels and the adaptability of existing combustion systems to different fuels. In many ECE countries, some coal or oil combustion plants are being replaced by gas-fired combustion plants. Dual-fuel plants may facilitate fuel switching.

(b) Fuel cleaning

Cleaning of natural gas is state-of-the-art technology and widely applied for operational reasons. Cleaning of process gas (acid refinery gas, coke oven gas, biogas, etc.) is also state-of-the-art technology. Desulphurization of liquid fuels (light and middle fractions) is state-of-the-art technology. Desulphurization of heavy fractions is technically feasible; nevertheless, the crude properties should be kept in mind. Desulphurization of atmospheric residue (bottom products from atmospheric crude distillation units) for the production of low-sulphur fuel oil is not, however, commonly practised; processing low-sulphur crude is usually preferable. Hydro-cracking and full conversion technology have matured and combine high sulphur retention with improved yield of light products. The number of full conversion refineries is as yet limited. Such refineries typically recover 80 per cent to 90 per cent of the sulphur intake and convert all residues into light products or other marketable products. For this type of refinery, energy consumption and investment costs are increased. Typical sulphur content for refinery products is given in table 1.

Current technologies to clean hard coal can remove approximately 50 per cent of the inorganic sulphur (depending on coal properties) but none of the organic sulphur. More effective technologies are being developed which, however, involve higher specific investment and costs. Thus the efficiency of sulphur removal by coal cleaning is limited compared to flue gas desulphurization. There may be a country-specific optimization potential for the best combination of fuel cleaning and flue gas cleaning.

(c) Advanced combustion technologies

These combustion technologies with improved thermal efficiency and reduced sulphur emissions include: fluidized-bed combustion (FBC): bubbling (BFBC), circulating (CFBC) and pressurized (PFBC); integrated gasification combined-cycle (IGCC); and combined-cycle gas turbines (CCGT).

Stationary combustion turbines can be integrated into combustion systems in existing conventional power plants which can increase overall efficiency by 5 per cent to 7 per cent, leading, for example, to a significant reduction in SO\textsubscript{2} emissions. However, major alterations to the existing furnace system become necessary.
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 additionally be reduced by integrated combustion control in the system due to the addition of lime/limestone to the bed material. The total installed capacity of FBC has reached approximately 30,000 MW\textsubscript{th} (250 to 350 plants), including 8,000 MW\textsubscript{th} in the capacity range of greater than 50 MW\textsubscript{th}. By-products from this process may cause problems with respect to use and/or disposal, 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. Sulphur emission control is achieved by the use of state-of-the-art technology for raw gas cleaning facilities upstream of the gas turbine. The technology also exists for heavy oil residues and bitumen emulsions. The installed capacity is presently about 1,000 MW\textsubscript{eL} (5 plants).

Combined-cycle gas-turbine power stations using natural gas as fuel with an energy efficiency of approximately 48 per cent to 52 per cent are currently being planned.

(d) Process and combustion modifications

Combustion modifications comparable to the measures used for NO\textsubscript{x} emission control do not exist, as during combustion the organically and/or inorganically bound sulphur is almost completely oxidized (a certain percentage depending on the fuel properties and combustion technology is retained in the ash).

In this annex dry additive processes for conventional boilers are 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, the Ca/S ratio is high and sulphur removal low. Problems with the further utilization of the by-product have to be considered, so that this solution should usually be applied as an intermediate measure and for smaller units (table 2).

(e) Flue gas desulphurization (FGD) processes

These processes aim at removing already formed sulphur oxides, and are also referred to as secondary measures. The state-of-the-art technologies for flue gas treatment processes are all based on the removal of sulphur by wet, dry or semi-dry and catalytic chemical processes.

To achieve the most efficient programme for sulphur emission reductions beyond the energy management measures listed in (i) above a combination of technological options identified in (ii) above should be considered.

In some cases options for reducing sulphur emissions may also result in the reduction of emissions of CO\textsubscript{2}, NO\textsubscript{x} and other pollutants.

In public power, cogeneration and district heating plants, flue gas treatment processes used include: lime/limestone wet scrubbing (LWS); spray dry absorption (SDA); Wellman Lord process (WL); ammonia scrubbing (AS); and combined NO\textsubscript{x}/SO\textsubscript{x} removal processes (activated carbon process (AC) and combined catalytic NO\textsubscript{x}/SO\textsubscript{x} removal).

In the power generation sector, LWS and SDA cover 85 per cent and 10 per cent, respectively, of the installed FGD capacity.
Several new flue gas desulphurization processes, such as electron beam dry scrubbing (EBDS) and Mark 13A, have not yet passed the pilot stage. Table 2 shows the efficiency of the above-mentioned secondary measures based on the practical experience gathered from a large number of implemented plants. The implemented capacity as well as the capacity range are also mentioned. Despite comparable characteristics for several sulphur abatement technologies, local or plant-specific influences may lead to the exclusion of a given technology. Table 2 also includes the usual investment cost ranges for the sulphur abatement technologies listed in sections (ii) (c), (d) and (e). However, when applying these technologies to individual cases it should be noted that investment costs of emission reduction measures will depend amongst other things on the particular technologies used, the required control systems, the plant size, the extent of the required reduction and the time-scale of planned maintenance cycles. The table thus gives only a broad range of investment costs. Investment costs for retrofit generally exceed those for new plants.

(Up to the Table of Contents)

IV. CONTROL TECHNIQUES FOR OTHER SECTORS

10. The control techniques listed in section 9 (ii) (a) to (e) are valid not only in the power plant sector but also in various other sectors of industry. Several years of operational experience have been acquired, in most cases in the power plant sector.

11. The application of sulphur abatement technologies in the industrial sector merely depends on the process’s specific limitations in the relevant sectors. Important contributors to sulphur emissions and corresponding reduction measures are presented in table 3 below.

12. In the sectors listed in table 3, process-integrated measures, including raw material changes (if necessary combined with sector-specific flue gas treatment), can be used to achieve the most effective reduction of sulphur emissions.

13. Reported examples are the following:

(a) In new kraft pulp mills, sulphur emission of less than 1 kg of sulphur per tonne of pulp AD (air dried) can be achieved;**
(b) In sulphite pulp mills, 1 to 1.5 kg of sulphur per tonne of pulp AD can be achieved;
(c) In the case of roasting of sulphides, removal efficiencies of 80 to 99% for 10,000 to 200,000 m³/h units have been reported (depending on the process);
(d) For one iron ore sintering plant, an FGD unit of 320,000 m³/h capacity achieves a clean gas value below 100 mg SO₂/Nm³ at 6 per cent O₂;
(e) Coke ovens are achieving less than 400 mg SO₂/Nm³ at 6 per cent O₂;
(f) Sulphuric acid plants achieve a conversion rate larger than 99 per cent;
(g) Advanced Claus plant achieves sulphur recovery of more than 99 per cent.

V. BY-PRODUCTS AND SIDE-EFFECTS

14. As efforts to reduce sulphur emissions from stationary sources are increased in the countries of the ECE region, the quantities of by-products will also increase.
15. Options which would lead to usable by-products should be selected. Furthermore, options that lead to increased thermal efficiency and minimize the waste disposal issue whenever possible should be selected. Although most by-products are usable or recyclable products such as gypsum, ammonia salts, sulphuric acid or sulphur, factors such as market conditions and quality standards need to be taken into account. Further utilization of FBC and SDA by-products have to be improved and investigated, as disposal sites and disposal criteria limit disposal in several countries.

16. The following side-effects will not prevent the implementation of any technology or method but should be considered when several sulphur abatement options are possible:

   (a) Energy requirements of the gas treatment processes;
   (b) Corrosion attack due to the formation of sulphuric acid by the reaction of sulphur oxides with water vapour;
   (c) Increased use of water and waste water treatment;
   (d) Reagent requirements;
   (e) Solid waste disposal.

VI. MONITORING AND REPORTING

17. The measures taken to carry out national strategies and policies for the abatement of air pollution include: legislation and regulatory provisions, economic incentives and disincentives; as well as technological requirements (best available technology).

18. In general, standards are set, per emission source, according to plant size, operating mode, combustion technology, fuel type and whether it is a new or existing plant. An alternative approach also used is to set a target for the reduction of total sulphur emissions from a group of sources and to allow a choice of where to take action to reach this target (the bubble concept).

19. Efforts to limit the sulphur emissions to the levels set out in the national framework legislation have to be controlled by a permanent monitoring and reporting system and reported to the supervising authorities.

20. Several monitoring systems, using both continuous and discontinuous measurement methods, are available. However, quality requirements vary. Measurements are to be carried out by qualified institutes using measuring and monitoring systems. To this end, a certification system can provide the best assurance.

21. In the framework of modern automated monitoring systems and process control equipment, reporting does not create a problem. The collection of data for further use is a state-of-the-art technique; however, data to be reported to competent authorities differ from case to case. To obtain better comparability, data sets and prescribing regulations should be harmonized. Harmonization is also desirable for quality assurance of measuring and monitoring systems. This should be taken into account when comparing data.

22. To avoid discrepancies and inconsistencies, key issues and parameters, including the following, must be well defined:

   (a) Definition of standards expressed as ppmv, mg/Nm³, g/GJ, kg/h or kg/tonne of product. Most of these units need to be calculated and need specification in terms of gas temperature, humidity,
pressure, oxygen content or heat input value;

- (b) Definition of the period over which standards are to be averaged, expressed as hours, months or a year;
- (c) Definition of failure times and corresponding emergency regulations regarding bypass of monitoring systems or shut-down of the installation;
- (d) Definition of methods for back-filling of data missed or lost as a result of equipment failure;
- (e) Definition of the parameter set to be measured. Depending on the type of industrial process, the necessary information may differ. This also involves the location of the measurement point within the system.

23. Quality control of measurements has to be ensured.

* Options (i) (a) and (b) are integrated in the energy structure and policy of a Party. Implementation status, efficiency and costs per sector are not considered here.

** Control of sulphur-to-sodium ratio is required, i.e. removal of sulphur in the form of neutral salts and use of sulphur-free sodium make-up.

(Up to the Table of Contents)

© UNECE 2000