Refining BREF review
– air emissions

Prepared by the CONCAWE Air Quality Management Group's Special Task Force on Integrated Pollution Prevention and Control (AQ/STF-70)

P. Béraud-Dufour
K. Bilinska
A. Buchsbaum
G. Chaput
P. Chetkowski
G. De Caluwé
K. den Haan
J.M. Fernandez
R. Ha
M. Konijn
J.-F. Larivé
F. Leotoing
G. Maheridou
A. Mendes
F. Oswald
L. Post
R. Söjtöri
L. White

P. Roberts (Technical Coordinator)

ABSTRACT

A review of emission and abatement technologies has been carried out to inform the review of the Reference Document for Best Available Techniques for the Mineral Oil and Gas Refining Industries (the BREF) which acts as a guidance to permit authorities when implementing the Industrial Pollution Prevention Control Directive.

This report extends and supplements CONCAWE Report no. 99/01 - Best Available techniques to Reduce Emissions from Refineries. Focus is on providing additional information on emissions to air, with new information on NO_x emissions from combustion, emissions from FCC units, sulphur removal and recovery and vapour recovery systems.

Recommendations are made as to how to improve the BREF and update the Associated Emission Levels (AELs) ascribed to each technique. It is suggested that the BREF be clearer in its definition of AEL values associated with the Best Available Technique by enumerating each component technique.

This work did not set out to gather detailed information on costs of abatement techniques because a substantial element of cost is in the local implementation and this is extremely difficult to quantify. However, where cost information has become available in the course of the work on techniques, it has been included.

KEYWORDS

IPPC, Best Available Techniques, BAT, Pollution, Control, Emission, FCCU, NO_x, Burner, Sulphur, Recovery, SRU, Vapour, Recovery, VRU, SO_x, Particulate, PM, TSP.

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CONTENTS

Page

SUMMARY

The IPPC Directive requires regulatory authorities to base operating permit conditions on Best Available Techniques (BAT). A technique may involve the application of technology or methodology or both. Advice on techniques and the Associated Emission Level (AEL) range associated with each technique is published in the Reference Document for Best Available Techniques for the Mineral Oil and Gas Refining Industry (hereafter the Refineries BREF or just BREF).

A criticism of the first version of the Refineries BREF may be that the quoted AEL ranges are insufficiently qualified and do not everywhere provide permitting authorities with appropriate guidance for their specific installations. Accordingly data collection and analysis will be an important part of the review.

This report documents a review by Concawe Special Task Force AQ/STF-70 of some key techniques considered to be Best Available Techniques (BAT) in the current first version of the Refineries BREF by process of critical review against available operating data. Key information and conclusions from this report will provide a useful data-based contribution to the review of the Refineries BREF.

Given the large scope of the Refineries BREF and taking into account available resources, it was decided to focus on the following key BATs mentioned in Chapters 4 and 5 of the BREF:

- Abatement of NO_x and SO_x and PM emissions from combustion,
- SO_2, NO_x and Particulate Matter (PM) emissions from Catalytic Cracking,
- Amine treating of refinery fuel gases,
- Sulphur recovery efficiency from Sulphur Plants
- Volatile Organic Compounds (VOCs) recovery from Vapour Recovery Units.

These techniques and processes were selected because of both their significance as emission sources and their widespread use in the refining industry.

Consistent with requirements defined by the EU authorities on the review of a BREF actual emission and operating data have been collected on the aforementioned techniques. These datasets formed the main basis for an evaluation of the current BREF. As a result of this review a relatively large number of amendments are proposed. These are primarily on the so called Associated Emission Levels (AELs) used by permit authorities as a basis for setting environmental permit limits but include also amendments on the applicability constraints of techniques and on cross-media effects.

Instead of defining single AEL values, which are inappropriate given the many different types of installed equipment and their different operating conditions, AEL ranges are proposed in most cases, drawn from a wide range of real plant observations. When considered justified, separate ranges are proposed for new facilities and retrofits or permit renewal of existing installations. Furthermore, the proposed AEL ranges are expected to cover the daily variations associated with normal plant operations, excluding start-up and shutdown conditions or any special activity of short duration. Where justified, more long-term averaging times are proposed, such as monthly based AELs.

The majority of the proposed AEL amendments relate to an increase of the upper AEL range for emission concentration parameters and (equivalently) the lower AEL range for emission reduction efficiencies. This is the case for Low NO_x burners, SCR and SNCR on both fired heaters and boilers and Catalytic Cracking Units, Sulphur Recovery Units, Amine Treating and to a lesser extent Vapour Recovery Units.

Two emerging techniques are discussed, NO_x reduction additives and third stage backflow filters for particulate control in catalytic cracking.

The consideration of a BAT also involves assessment of the implied cost and of the environmental benefits expected to be achieved.

Financial data have not been deliberately gathered as part of this review because site specific retrofit components are a very significant fraction of the overall cost of implementing a technique. Completely new "green or brown field" installations, for which costs might be estimated from suppliers data, are not typical of the European industry and so manufacturers data alone is insufficient, and potentially misleading, as a reference.

The IPPC Bureau has (in December 2008) initiated a data collection exercise that might inform on these issues asking as it does for very detailed site information to be obtained through the permitting authorities.

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1.   INTRODUCTION

The Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries [1], further referred to as 'BREF', was issued in February 2003. In line with the current IPPC Directive (96/61/EC) it serves as a reference for permit authorities to define environmental permit limits and conditions. The BREF provides extensive technical background information on the European refining industry and on refining processes and technologies. We consider two chapters to be especially relevant to permitting. Chapter 4 describes techniques to be considered in the determination of BAT (Best Available Techniques) and documents AEL ranges per pollutant for each technique. Chapter 5 draws principal conclusions about BAT and the associated emission levels (AELs) and then defines AEL ranges for each relevant pollutant per type of refinery process unit, thereby indicating that the AEL ranges are to be achieved by a suitable combination of BATs.

AEL ranges are defined by a minimum and maximum value, either as an emission concentration, a mass emission per unit of production or as any other environmental performance parameter such as a percentage emission reduction. Unless otherwise specified AELs are defined in the BREF as daily averages.

Although the BREF contains an extensive list of BATs, the intention of the IPPC Directive is not to impose techniques as such, but to ensure that permit limits are based on AEL ranges as far as is needed to achieve EU and local environmental goals. BAT is not exclusive, if other techniques, not listed in the BREF, perform within the BREF AEL range, then they may also be considered a BAT application.

The AEL ranges given in Chapter 5 of the BREF are intended to represent expected emission performance. In the absence of supporting data for the ranges in the first BREF version they have sometimes been interpreted as Emission Limit Values to be applied at all times and not including a realistic margin to account for the normal variability in the process operation. In that context the AEL values should be referenced to averaging times. Users of the BREF should be aware that the AEL ranges may not be appropriate for different averaging times. Examples of averaging times might be: daily average, average over an operating cycle in the case of catalytic processes, short term upset conditions etc.

Furthermore, the BREF documents information on applicability of techniques, limitations with respect to operability or restrictions with regard to implementation in retrofits of existing facilities. Finally, the BREF contains information on cross media effects, such as energy consumption of techniques, other environmental impacts, and costs.

The current Refineries BREF has been compiled based on information made available by various stakeholders, including EU authorities, member state delegates, NGOs, technology providers and the refining industry represented by CONCAWE. The basis for the input from CONCAWE in the first BREF process is documented in CONCAWE Report 99/01 [2].

CONCAWE also issued another report 4/03 [3] providing guidance to users of the Refineries BREF.

Although part of the information contained in CONCAWE Report 99/01 was incorporated into the first BREF version, there is still a considerable number of AEL ranges in the BREF that are not backed by real plant data, but are rather based on

general information which may not reflect actual operational conditions. This is believed to explain the considerable number of 'split views' between the Technical Working Group (TWG) stakeholders. These split views are documented in the BREF and represent different opinions about those BREF AEL ranges for which no consensus had been reached at the time. Furthermore, AEL ranges are not always clearly explained in terms of which operating conditions or design parameters determine the position of a certain BAT application in the AEL range.

These shortcomings have recently been addressed in a Position Paper of the EU Information Exchange Forum (IEF) [4]. As a main recommendation this paper concluded that BREF AEL ranges ought to be better underpinned by real plant data, including technical information which will enable the positioning of BAT performance within the AEL range. CONCAWE fully supports this view and the IEF recommendation has been a driving force for this work.

2. OBJECTIVES

In order to address the objectives formulated in the IEF Position Paper, a CONCAWE Task Force, STF-70, was set up. Given the large scope of the Refining BREF and taking into account available resources, STF-70 has decided to focus on the following key BATs mentioned in Chapters 4 and 5.

- Abatement of NO_x emissions from combustion
- SO_2, NO_x and Particulate Matter (PM) from Catalytic Cracking
- Amine treating of refinery fuel gases
- Sulphur recovery efficiency from Sulphur Plants
- Vapour Recovery Units

These techniques and processes were selected based on their significance as emission sources and also based on their widespread use in the refining industry.

As a main task, STF-70 has collected actual emission and operating data on abatement technique performance from real plants, and evaluated the BREF AELs and their averaging times in the context of these data. When considered justified in the light of the observed real performance, amendments to the BREF are proposed.

Furthermore, technical background information has been provided to better position performance of techniques in the AEL ranges, taking into account variable operating conditions, equipment design characteristics and retrofit applications.

The analysis has allowed STF-70 to propose amendments on the applicability of BATs and also in some cases to provide data or information on cross media effects.

The consideration of a BAT also involves assessment of the implied cost-effectiveness and of the environmental benefits expected to be achieved. Financial data have not been gathered as part of this review primarily because site specific retrofit components are a very significant fraction of the overall cost of implementing a technique. Completely new "green or brown field" installations, for which costs might be more easily estimated from suppliers data, are not typical of the European industry and so manufacturer's data alone is insufficient, and potentially misleading, as a reference.

3.   METHODOLOGY

Datasets from existing individual plants have been collected, containing emission records preferentially based on continuous emission analyzers but also relevant operating conditions and process or equipment design parameters. In most cases hourly average values have been obtained during a period of several months of routine plant operation.

All datasets are stored in an anonymous mode at a CONCAWE intranet site only accessible to the STF-70 members.

The work for Sulphur Recovery Units has been outsourced to the consultancy company Sulphur Experts. Their work is documented in a separate report [6], but the key findings have been summarized in this report (see Chapter 7).

Datasets have been selected to represent a whole range of application of a certain technique, thereby looking at differences in operating conditions and equipment design. Consequently, the datasets cover a wide range of environmental performance levels. Importantly the majority of datasets represent retrofit cases, which, given the maturity of the refining industry, are more relevant than new build examples.

Emission ranges have been derived from each dataset using a statistical approach in which the daily average value and the 95% variability range were determined. Data analysis has been carried out to understand the variability by taking into account the effect of different process operating conditions on the emission performance.

In this way all datasets are evaluated in the context of the BREF AEL range. Based on the outcome of this evaluation, amendments are proposed to the AEL ranges and/or averaging times when considered justified. It should be noted that the analysis has been based on the assumption that AELs are applicable only to normal operations, therefore excluding start up and shutdown conditions or any special operations of short duration such as soot-blowing, steam-air decoking or sand scouring of heat transfer surfaces. Furthermore, AELs are proposed for each BAT technique and not for any combination of techniques as is the case in the current BREF, e.g. for NO_x from combustion. When available, and considered justified, information has been provided on applicability and cross media effects. At no point in the process has aggregation of data been carried out.

4. COMBUSTION NO$_X$

In this chapter the current BREF is evaluated and amendments are proposed for the following techniques:

- Low NO$_x$ burners on fired heaters and boilers

- SCNR and SCR on fired heaters and boilers.

NO$_x$ reduction techniques for turbines or other engines are not included in the scope of this report.

4.1. LOW NO$_X$ BURNERS ON FIRED HEATERS AND BOILERS

4.1.1. Introduction and background information

NO$_x$ from fixed combustion sources consists of three components, 'Thermal' NO$_x$, 'Fuel' NO$_x$ and to a lesser extent 'Prompt' NO$_x$. NO$_x$ generated from combustion sources predominantly consists of NO (95%), while the balance is NO$_2$. In the BREF NO$_x$ emission concentrations from fired heaters and boilers are expressed as mg of NO$_2$ equivalent per Nm^3 of dry gas at 3% excess oxygen, unless defined otherwise. In this report emission concentrations are expressed on the same basis.

Thermal NO$_x$ derives its name from the thermal fixation of molecular nitrogen and oxygen from the combustion air at high temperatures. It is the predominant source of NO$_x$ from gas fired systems. NO$_x$ generated in this way is highly dependant on peak flame temperatures and to a lesser extent on oxygen availability. Parameters which increase flame temperature, therefore increase thermal NO$_x$. These include fuel parameters (fuel H$_2$ content, fuel hydrocarbon molecular weight), firebox temperatures and the use of air preheat. Thermal NO$_x$ is increased by increasing excess air, up to a maximum value beyond which the effect of flame temperature becomes dominant.

Fuel NO$_x$ derives its name from the oxidation of nitrogen chemically bound with the fuel. Fuel NO$_x$ is mostly dependent on the type and quantity of fuel-bound nitrogen and on oxygen availability in the flame front. In general, Fuel NO$_x$ increases proportionally with fuel-bound nitrogen content and with oxygen availability in the flame front. Fuel NO$_x$ can be the predominant source of NO$_x$ when firing heavy hydrocarbons under conditions that limit the production of thermal NO$_x$. Generally liquid fuels contain bound nitrogen. Fuel gas may contain ammonia and molecular nitrogen. The ammonia present in fuel gas takes part in Fuel NO$_x$ formation, whereas the molecular nitrogen in the fuel does not. It is not distinguishable from molecular nitrogen in the combustion air.

Prompt NO$_x$ is the term used to define NO$_x$ that is generated from intermediate species formed under high temperature fuel rich conditions. The principal formation mechanism is the reaction between molecular nitrogen from the combustion air and the hydrocarbon in the fuel; generating intermediate species (for example HCN). Further reaction with oxygen generates NO$_x$. This NO$_x$ is predominantly influenced by burner design and fuel composition. In general, prompt NO$_x$ formation is increased within a burner that is air staged (higher concentration of fuel species) and when using heavier hydrocarbons such as propane and above.

It is generally accepted that Prompt NO_x only accounts for low absolute emissions and represents a very small fraction of the total NO_x emissions from combustion units without NO_x control features. However, as Prompt NO_x is only marginally reduced (and may be favoured) in low NO_x burner designs, it represents a larger fraction of the total emissions of low NO_x burners.

Low NO_x burners are available in a variety of forms. In essence, the prime objective is to reduce the peak flame temperature and minimise conditions for the reaction of nitrogen in the combustion air with excess oxygen. This is accomplished by staging the combustion process by which we mean progressively adding fuel to air or vice versa. Burners can therefore either be fuel staged or air staged. Air staging is the main NO_x control technique for liquid fuels, because the complexity of liquid fuel atomization generally precludes having multiple atomizers in a single burner. Furthermore improved NO_x reduction performance is obtained for liquid firing when the oxygen concentration near the fuel is reduced as is achieved in an air staged burner.

As Low NO_x burner technology has progressed, the total NO_x emitted by these groups of burners has been further reduced by adding supplementary techniques, such as internal flue gas recirculation, induced by the flow of either combustion air or fuel. These techniques are inherent to the burner design. There is a further technique, external flue gas recycling, which requires the installation of additional flue ducting outside the firebox and the collection and physical reinjection of combustion products. Wherever this document refers to flue gas recycle the meaning is internal flue gas recycling.

It must be recognized that operating parameters play a variable role in NO_x formation and can influence the performance of a low NO_x burner so that in the course of normal use NO_x emissions will vary and no single NO_x emission level can be attributed to one burner and, even more importantly, not to one burner type. Actual NO_x emissions in industrial fired heaters and boilers will be affected by the oxygen concentration in the combustion chamber, the combustion chamber temperature, the spacing and possible interaction between neighbouring flames, furnace geometry, number and size of burners, air preheat and heat density. This explains why burners may emit wide ranges of NO_x in different industrial applications.

In determining the retrofit suitability of low NO_x burners, the specific application needs to be reviewed. Low NO_x burners by their very nature of delayed combustion tend to have a wider and/or longer flame compared to traditional burners. Furthermore, greater spacing between these burners is generally required to avoid flow interactions within the firebox, which can impact on the NO_x reduction performance, heat distribution and flame profile. For retrofit applications, where the geometry of the firebox is predetermined, the low NO_x burner flame may not physically fit the firebox without derating the unit. The upper end of the achievable NO_x emission range is expected to be higher in retrofit applications compared to new units. For new applications, the combustion chamber can be designed around the low NO_x burner, to provide the necessary spacing around burners and to fit the increased flame dimensions and therefore a narrow range and improved predictability of NO_x emissions would be expected.

Other parameters, specific to the application, are fuel quality and process requirements, which can affect the firebox temperature. The wide variety of applications results in an overall wide NO_x emission range for each type of Low NO_x

burner, for this reason it is important to qualify the application when assessing what is a reasonable associated emission value range for an installation.

Extensive work has been undertaken to develop correlations that relate NO_x emissions to changes in operational parameters (e.g. fuel type/composition, combustion air preheat temperature and firebox temperature). While this has largely been driven by the desire to provide a robust estimate of NO_x emission levels in a given situation, the availability of such correlations provide helpful input to the establishment of AEL ranges. In the Netherlands, such correlations have been incorporated into the regulatory framework [11] as "adjustment factors" to the "Base ELVs" for NO_x for use in the permitting process. This approach is described in Appendix I. However, it is worth noting here that the resulting adjustment factors are significant: For example in moving from a situation of "no" to "high" combustion air preheat, the adjustment factor is more than 2; for moving from a "low" to "high" firebox temperature the adjustment factor is more than 1.5. As indicated above, this has important implications for the setting of BAT AEL ranges. This will be further elaborated in the discussion on proposed amendments to the BREF (Section 4.1.3).

Often new burners are tested on a manufacturer's combustion test facility to verify capacity, operating stability and determine initial NO_x emission estimates. The NO_x emissions observed on a test facility can vary widely from those observed in a real plant. In general, a single burner is only tested on simulated fuels under very controlled conditions. In the real combustion plant however, the applications tend to vary as the installation includes multiple burners with varying gas and liquid fuel compositions. Several attempts have been made by the manufacturers to assess a so called 'rig factor' to compare test facility NO_x emissions with the real plant. However, due to the wide disparity of applications, these have had limited success. In many applications the real plant emission exceeds values guaranteed by the manufacturer.

For the purpose of this report the different low NO_x burner technologies developed over time can be categorized into four main groups:

- *Gas fired staged fuel / staged air (Gas LNB)*

This earliest group of LNB achieved NO_x reduction by basic staging of fuel or air between the inner primary zone of the burner and the perimeter of the burner, controlling the rate at which heat is liberated from the fuel and hence the flame temperature.

A typical range of NO_x emissions achieved with this burner type with the combustion air at ambient temperature is 80–140 mg/Nm^3.

Some burners within this category incorporated a low level of flue gas recirculation to reduce oxygen concentration in the inner zone. Application of this extension to the technology results in a longer flame length compared to the previous category. Applicability to retrofit applications must be carefully reviewed.

- *First Generation Gas fired Ultra Low NO_x burners (ULNB)*

These burners in general are of the staged fuel type but with a higher level of flue gas recirculation. The level of fuel staging is similar to that used in the Gas LNB above.

A typical range of NO_x emissions achieved with this burner type with the combustion air at ambient temperature is 60–90 mg/Nm^3.

- *Latest Generation Gas fired Ultra Low NO_x burners (ULNB)*

  These burners are designed for a higher degree of fuel staging, generally incorporating internal flue gas recirculation and an increased number of gas injectors. This results in a decrease in the diameter of individual gas jets making them more prone to plugging and coking but also increasing the risk for flame instability, which could lead to flame out. To avoid plugging problems, coalescing filters and heat tracing of the fuel gas supply piping are often required when burning refinery gas. Some applications have also used stainless steel piping downstream of the filters. To mitigate the risk of flame instability the diameter of the gas jets has to stay above a certain minimum, depending upon the application.

  Applicability is limited to fuel gases having a limited amount of components heavier than propane and a low olefinic content. Compared to the other gas fired burner types NO_x performance is more sensitive to excess oxygen. Control of the oxygen concentration in the firebox helps to achieve lowest NO_x emissions. However, steady automatic oxygen control on existing natural draft furnaces is often not feasible, reliable or safe,

  Due to the fact that these burners are designed to achieve lower NO_x emissions compared to the other burner types the sensitivity towards fuel-bound nitrogen increases. Therefore some of the claimed emission ranges for these burners can not be met if the fuel gas contains a measurable quantity of nitrogenous gases such as ammonia.

  A typical range of NO_x emissions achieved with this burner type firing with combustion air at ambient temperature and firebox temperatures below 900°C is 30–60 mg/Nm^3.

- *Dual fired low NO_x burners*

  These burners are designed for single liquid fuel firing or for mixed liquid and gas firing. Usually these burners are also designed to allow single gas firing. While liquid fuel can be staged somewhat to reduce fuel NO_x there are fewer options on these burners to reduce thermal and prompt NO_x when compared to a gas only burner.

  A typical range of NO_x emissions achieved with this burner type with the combustion air at ambient temperature is 80–140 mg/Nm^3.

  A particular problem with heavy fuel oil firing is that incomplete combustion results in the emission of coke particles and poor fuel/air mixing can give rise to the emission of smoke (soot). As fuel/air mixing is the primary NO_x control it is found that emissions of NO_x and carbon particles from liquid fuel firing are generally inversely proportional. The difficulty in designing an oil fired burner with low NO_x performance is that it generally results in increased particulates generation and will be more prone to coking or oil dripping.

  There is no US experience with these burners. European experience is still limited, and success rates in the EU are mixed.

4.1.2. Discussion of BREF

4.1.2.1. Current BREF associated emission ranges and limits

The Associated Emission ranges and Limits (AEL) for NO_x emission from low NO_x burners and combustion in the current BREF can be summarized as follows:

BREF paragraph	Fuel type	NO_x emission, mg/Nm^3 @ 3% O_2 dry on fired heaters and boilers	Averaging time	Comments
4.10.4.1	Refinery fuel gas	30-150	Daily	
	Liquid refinery fuel (0.3% N)	100-250	Daily	
	Heavy liquid refinery fuel	150-400	Daily	
5.2.10	Gas fired	20-150	Daily	(1)
	Liquid fired	55-300	Daily	(2)

(1): To be achieved by applying suitable combination of different Best Available Technology (BAT) (low NO_x burners, Selective Catalytic Reduction (SCR), Selective Non Catalytic Reduction (SNCR,). The lower end of range reflects natural gas firing.

(2): To be achieved by applying suitable combination of different BAT (low nitrogen fuel, low NO_x burners, SCR, SNCR).

Furthermore paragraph 5.2.10 contains an AEL range of 5-20 mg/Nm^3 on particulate emissions from combustion, to be achieved by a suitable combination of reducing fuel consumption, maximising the use of gas and low ash content liquid fuels, steam atomisation on liquid fuels and ESP or filters in the flue gas of furnaces and boilers when heavy liquid fuel is used.

4.1.2.2. Discussion of supporting real plant data

24 datasets have been collected. All are retrofit applications:

- 6 related to fired heaters on staged fuel Ultra Low NO_x burners
- 6 related to gas fired heaters on staged air LNB
- 7 related to gas fired heaters on staged fuel LNB
- 5 related to dual (liquid/gas) fired heaters on LNB

The figures 1 and 2 below reflect these datasets and provide an overview of their measured NO_x performance, expressed as mg NO_x per Nm^3 dry flue gas at 3% O_2 in accordance with the requirements of the Bref. In the graphs each dataset is represented by 3 parameters for NO_x:

- Maximum value
- Minimum value
- Median value

These values are derived from either continuous emission measurements or from discontinuous emission measurements, whichever are available.

For gas fired combustion units the graphs also represent the air preheat temperature level associated to each dataset. This shows to be a very significant parameter affecting NO_x for this category.

For dual fired combustion units, the proportion of liquid firing and the nitrogen content of the liquid fuel (in % w) are selected as the prime operating parameters. It should be noted that the notion 'dual firing' in this report reflects an operation where gaseous and liquid fuels are burnt simultaneously in the same burner.

Other relevant operating parameters or burner and combustion unit characteristics are included in **Tables 4-1** to **4-4**. The flue excess oxygen content is not included because all datasets represent a combustion operation at about 3% O_2.

Fig. 4-1 NO_x for gas fired heaters and boilers
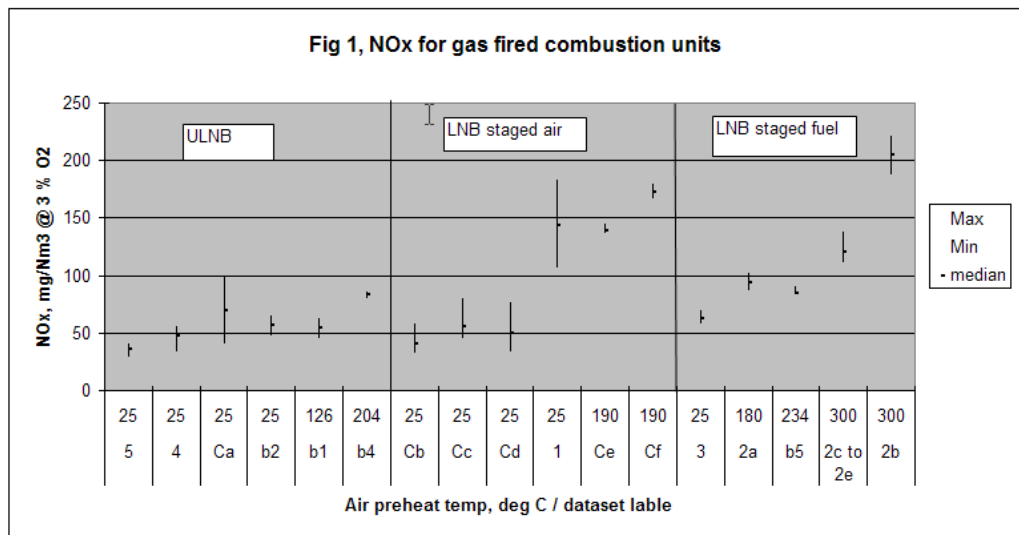
Fig. 4-2 NO_x for dual fired heaters and boilers
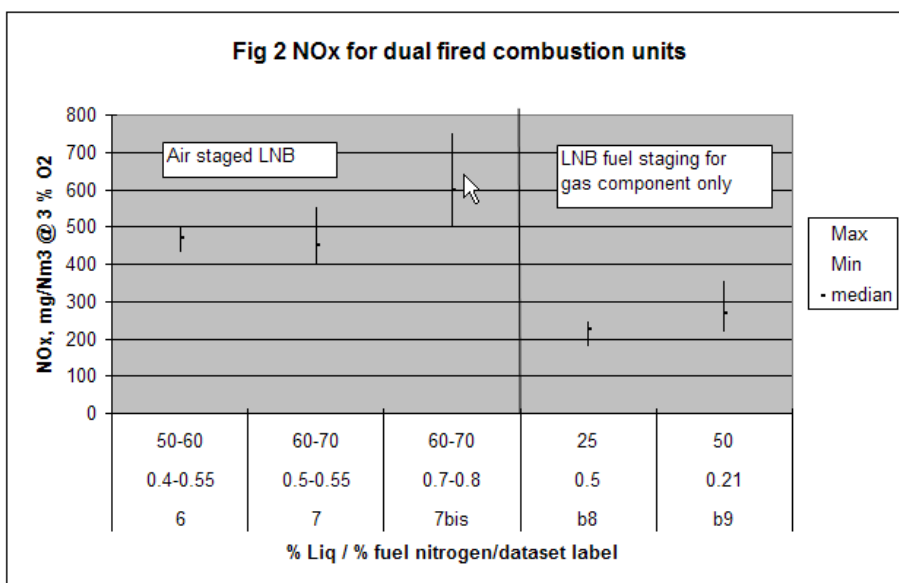
In the following tables the key observations are summarized for each dataset. The identification of the datasets in the tables corresponds to the tags on the graphs: **Figures 4-1** and **4-2**.

Table 4-1 Gas Fired ULNB

ID	CEMS (1) (Y/N)	H_2 content Fuel gas, vol %	Comments
5	Y	40-60	• Light fuel gas: no C4+, max. 10% vol. C3. • Stainless steel fuel gas piping with coalescing filters. • NO_x is very sensitive to presence of fuel-bound nitrogen or ammonia in the fuel gas.
4	Y	40-60	• Light fuel gas: no C4+, max. 10% vol. C3. • Fuel gas piping equipped with coalescing filters. • NO_x is very sensitive to presence of fuel-bound nitrogen or ammonia in the fuel gas.
Ca	Y	17	• High radiant heat density, this could explain the higher NO_x level, despite no air preheat.
b2	Y	43	• No specific comments
b1	Y	43	• No specific comments
b4	N	10	• No specific comments

(1) CEMS: Continuous Emission Monitoring System. If 'no' data are based on discontinuous measurement.

Table 4-2 Gas Fired Air Staged LNB

ID	CEMS (1) (Y/N)	H_2 content Fuel gas, vol %	Comments
Cb	Y	17	• No specific comments
Cc	Y	17	• No specific comments
Cd	Y	17	• No specific comments
1	Y	40-50	• Specific heater lay-out: burners located next to internal dividing wall resulting in hotter flue gas recirculation.
Ce	N	20-45	• No specific comments
Cf	N	20-45	• No specific comments

(1) CEMS: Continuous Emission Monitoring System. If 'no' data are based on discontinuous measurement.

Table 4-3 Gas Fired Fuel Staged LNB

ID	CEMS (1) (Y/N)	H₂ content Fuel gas, vol %	Comments
3	Y	40-60	• Operates at 75% of design load
2a	N	40-50	• No specific comments
b5	Y	10	• No specific comments
2c- 2e	N	40-50	• No specific comments
2b	N	40-50	• Flame length limited by vertical firebox height.

(1) CEMS: Continuous Emission Monitoring System. If 'no' data are based on discontinuous measurement.

Table 4-4 Dual Fired Gas/liquid LNB

ID	CEMS (1) (Y/N)	Air preheat temp. °C	Comments
6	N	130	• Liquid fuel is heavy distillation residue • Air staged burners
7	Y	250	• Liquid fuel is heavy distillation residue • Air staged burners
7bis	Y	250	• Liquid fuel is heavy distillation residue • Air staged burners
b8	N	25	• Fuel staged for gaseous fuel • Air staged for liquid fuel
b9	N	25	• Fuel staged for gaseous fuel • Air staged for liquid fuel

(1) CEMS: Continuous Emission Monitoring System. If 'no' data are based on discontinuous measurement.

4.1.2.3. Conclusions derived from plant data

From the observations outlined in the above graphs and tables, the following conclusions can be made regarding the BREF AELs. Unless specified otherwise all AEL ranges discussed below are based on daily averages.

a. Gas fired low NOₓ burners

- The upper part of the Chapter 4 AEL range (30-150 mg/Nm³) is in some cases not achievable in retrofit applications due to specific design and construction characteristics of the existing combustion installation, such as:

  o Firebox dimensions limiting the flame size and therefore impeding to design and operate a LNB to its maximum performance. This is demonstrated by dataset 2b.
  o Specific location of the burners in the firebox, e.g. if burners are installed adjacent to an internal dividing wall, the flue gas which is re-circulated through the burner could be relatively hot, therefore increasing the NOₓ emission. This is demonstrated by dataset 1.

In all these cases a major retrofit would be required to achieve the upper AEL. Major retrofits in this regard would imply modifications with a scope similar to replacing the entire combustion plant or installing SCR units. These observations and conclusions confirm the comments made in the BREF, paragraph 4.10.4.1 on the technical limitations of retrofit applications.

- The performance of a LNB is very dependent upon the air preheat. At high air preheat temperature ranges (above a level of about 200°C) the emission performance is at the upper end of the Chapter 4 AEL range, as demonstrated by datasets 2c-2e for fuel staged LNB and by datasets Ce and Cf for air staged LNB. It should be noted that sacrificing air preheat to reduce the NO_x emissions concentration below the upper AEL is not to be considered a beneficial measure, as it results in a lower energy efficiency; thereby increasing fuel use and emissions of CO_2.

- The lower Chapter 4 AEL range of 30-50 mg/Nm^3 can be achieved in some applications of the most recent Ultra Low NO_x burner technology as demonstrated by datasets 5 and 4. However, this level of performance is only technically achieved without air preheat and for natural gas and light fuel gases containing no ammonia or any fuel-bound nitrogen. Light fuel gases in this respect means gas containing a limited quantity of saturated hydrocarbons heavier than propane or olefinic hydrocarbons. Additionally, to eliminate particles or droplets that might plug the primary burner ports, extensive fuel gas cleaning systems (such as coalescing filters) and/or heat tracing of the fuel gas supply piping, and in some cases stainless steel piping downstream of the filters, are required. There may be issues with flame stabilisation, depending upon the application, preventing NO_x levels in the 30-50 mg/Nm^3 range from being achieved. Additionally, because this low level of NO_x precludes the application of air preheat, energy efficiency gains cannot be realised and CO_2 emissions are increased.

- Replacing refinery fuel gas by natural gas firing is not considered an effective measure as it would result in an excess of refinery fuel gas, for which there would be no other outlet than destruction in the flare. Most datasets on fuel staged ULNB achieve a NO_x emission in the 50-100 mg/Nm^3 range.

- The lower Chapter 5 AEL of 20 mg/Nm^3 is not achievable by any currently available commercial gas-fired low NO_x burner technology alone. The best expected, but not guaranteed, burner vendor emission level is 35 mg/Nm^3 subject to the above constraints on fuel choice and operation.

In Appendix I the "Adjustment Factor" approach as used in the Netherlands to account for the key operational variables is applied to the median values of the full data set using the data in **Tables 4-1** to **4-3**. This demonstrates that most of the variability in median emission levels across the full data sets is accounted for by the variations in fuel composition, combustion air preheat and firebox temperature/intensity. The work also confirms the conclusion above that an appropriate BAT AEL range for low NO_x burner technology which accounts for operational variability is 50-200 mg/Nm^3.

The low end of the range corresponds to a situation where ultra low NO_x burners are operating with no air preheat, a low hydrogen content refinery fuel and in a moderate temperature firebox.

The high end of the range corresponds to a situation where low NO_x burners are operating at a high level of air preheat, high hydrogen content refinery fuel and in a high temperature firebox.

To emphasis the importance of connecting the technology to the particular operational situation, the adjustment factor approach would indicate that if ultra low NO_x burner technology were applied to the second situation the achievable emission level would only be 160 rather than 50 mg/Nm^3.

b. Dual liquid/gas fired low NO_x burners

- The Chapter 4 AEL range of 150-400 mg/Nm^3 for heavy liquid firing cannot be achieved with current dual fired low NO_x burner technology when burning heavy distillation residue liquid fuel. A level of 450 mg/Nm^3 can be achieved if heavy residue firing is limited to the order of 50% and if the fuel-bound nitrogen content is limited at or below 0.4% to 0.5% as demonstrated by datasets 6, 7, and 7bis. The above observation only reflects datasets representing applications without technical constraints such as: firebox dimensions in retrofit cases or a high level of air preheat. Datasets b8 and b9 confirm the above observation as these are either low on the amount of liquid fuel firing or on the nitrogen content of the liquid fuel.

- There is no data available to support the technical feasibility of the AEL range of 100-250 mg/Nm^3 for liquid refinery fuel firing with a nitrogen content of 0.3 wt %. It is expected that this AEL range is not technically feasible with any liquid fuel heavier than diesel and with some gas co-firing. A study carried out in the Netherlands [5] indicates that 71-201 mg/Nm^3 NO_x is achievable on firing a gas-oil type of fuel with a fuel-bound nitrogen content between 0.01 and 0.03%.

- We conclude that the Chapter 5 AEL range of 55-300 mg/Nm^3 is not achievable with current dual fired low NO_x burner technology fired with heavy fuel oil (with a fuel-bound nitrogen content between 0.3 and 0.8 wt %). The higher end of that AEL range would require the use of a light liquid fuel with a fuel-bound nitrogen content below 0.03% wt. The low end of the range is not considered technically feasible with current low NO_x burner technology and would require further technical abatement measures.

- Discontinuous PM emission measurements carried out on the combustion units represented in datasets 6,7 and 7bis resulted in a total PM emission level between 30 and 50 mg/Nm^3 at 50% to 60% heavy liquid firing. This translates into a level of up to 100 mg/Nm^3 for a unit firing 100% heavy liquid fuel, characterized by an ash content of around 0.05 wt % and an asphaltene content above 10% wt assuming a linear scaling. Consequently the Chapter 5 AEL range for particulate matter of 5-20 mg/Nm^3 (which applies to 100% liquid) is not achievable on this type of fuel, even not when firing down to the 50% breakpoint used in the majority fuel concept of the current LCP Directive. Application of this heavy fuel type would require post flue gas treatment such as electrostatic precipitators or other emission abatement techniques.

  As for gas firing, in Appendix I the "Adjustment Factor" approach to account for the key operational variables is applied to the median values of the full data set using the data in **Table 4-4**. This demonstrates that most of the variability in median emission levels across the data sets is accounted for by variations in fuel mix, fuel composition, combustion air preheat and firebox temperature/intensity. The work again confirms the conclusion above that an appropriate BAT AEL range for dual

fuel fired low NO_x burner technology which accounts for operational variability is 300-450 mg/Nm^3 where the fuel mix is 50% or more liquid firing consistent with the majority fuel concept of the Large Combustion Plant Directive.

The low end of the range corresponds to a situation where low NO_x burners are operating with no air preheat, a low nitrogen content refinery fuel and in a moderate temperature firebox.

The high end of the range corresponds to a situation where low NO_x burners are operating at a high level of air preheat (but <200°C), high nitrogen content refinery fuel (but <0.5% w/w) in a high temperature firebox.

To emphasis the importance of connecting the technology to the particular operational situation, the adjustment factor approach would indicate that if, in the second case, low NO_x burner technology were applied to a situation where the air preheat temperature was 300°C and the nitrogen content in the refinery fuel oil was 0.7%, the achievable emission level would be 550 rather than 450 mg/Nm^3. If the percentage of fuel oil fired rises to 70% (c.f. 50%) then the achievable emission level is limited to 690 mg/Nm^3 according to this adjustment factor approach. It is worth emphasising that these differences in achievable emission levels are a consequence of changes in operating conditions using exactly the same low NO_x burner technology.

4.1.3.   Proposed amendments to the BREF

Based on the conclusions describe above following amendments are proposed:

a. Paragraph 4.10.4.1

- The Upper AEL range (150 mg/Nm^3) on gas firing is not achievable for all existing applications with staged air or staged fuel LNB at an air preheat temperature above about 200°C. Sacrificing air preheat to reduce the NO_x emission concentration below the upper AEL is not to be considered an effective measure as it results in a lower energy efficiency, thereby increasing CO_2 emissions. Therefore it is proposed to increase the upper AEL range for retrofit applications to 200 mg/Nm^3 for burners using air preheat of up to 200°C.

- Based on the above observations and conclusions on the performance of ULNB, it is proposed to increase the lower AEL from 30 to 50 mg/Nm^3 for gas burners fired on refinery fuel gas. The very low level of 30 mg/Nm^3 is only achievable with latest generation Ultra Low NO_x burners under narrow circumstances:

  a) Fired by natural gas or light gas (without C3+) without any ammonia or fuel-bound nitrogen. Replacing refinery fuel gas by natural gas firing is not considered an effective measure as it would result in an excess of refinery fuel gas for which there would be no other outlet than destruction in the flare.

  b) Fuel gas cleaning systems are provided, such as coalescing filters and/or heat tracing of the fuel gas supply piping and in some cases stainless steel piping downstream of the filters.

  c) With precise control of the oxygen concentration at the firebox outlet for forced draft applications. This may not be feasible for natural draft applications.

d) No flame instability is encountered for the specific application.

- The best expected, but not guaranteed, burner vendor emission level is 35 mg/Nm^3. This low level of NO$_x$ precludes the application of air preheat; thereby reducing energy efficiency and increasing CO$_2$ emissions. It should be noted that a reduction of 20°C air preheat is equivalent to a 1% decrease in energy efficiency.

- Based on the observations and conclusions on the performance of dual firing LNBs it is proposed to replace the current AEL range of 150-400 mg/Nm^3 for heavy liquid refinery fuel by 300- 450 mg/Nm^3, applicable to a liquid firing rate of 50-100%, consistent with the majority fuel concept of the current LCP Directive. It is also proposed to include a comment that this is only achievable for liquid fuels with a fuel-bound nitrogen content below 0.5 wt %.

- The current AEL range of 100-250 mg/Nm^3 for liquid refinery fuel firing should refer to light liquid fuels (gasoils) only, with a fuel-bound nitrogen content at or below 0.01 wt%.

b. Paragraph 5.2.10

Chapter 5 currently sets a BAT AEL range based on a 'suitable combination of techniques'. It is proposed to provide a separate Chapter 5 AEL range for each technique. Consequently the proposed AEL ranges above are to be regarded BAT for Low NO$_x$ burners instead of NO$_x$ from combustion.

NOTE: The effect of operating conditions, air pre-heat temperature, bridge temperature and fuel composition can greatly influence where a burner emission falls in the AEL range. A full methodology for accounting for these effects is described in Appendix I.

- It is proposed to align the AEL range for gas firing to the range proposed above for Chapter 4: 50-150 mg/Nm^3 for new facilities and 50-200 mg/Nm^3 for retrofits, all based on daily averages and for the sole use of low NO$_x$ burners with qualification according to the fuel in use and the application of air preheat.

- It is proposed to change the AEL range for liquid fuel firing for new installations from the current 55-300 mg/Nm^3 to 300-450 mg/Nm^3 on a daily average basis, applicable to a liquid firing rate of 50-100%, consistent with the majority fuel concept of the current LCP Directive. It is also proposed to include a comment that this is only achievable for liquid fuels with a fuel-bound nitrogen content below 0.5 wt %. This AEL range is proposed to be applicable to the sole application of BAT 'Low NO$_x$ burners', instead of to 'NO$_x$ from combustion'.

- It is proposed to change the current AEL range for PM from 5-20 mg/Nm^3 to a range of 5-50 mg/Nm^3, applicable to a liquid firing rate of 50-100%, consistent with the majority fuel concept of the current LCP Directive and to include a comment that this is only achievable for liquid fuels with an asphaltene content below 10% and ash content below 0.05% wt. This AEL range is proposed to be applicable to the sole application of BAT 'Low NO$_x$ burners', instead of to 'NO$_x$ from combustion'. Furthermore, it should be noted that with oil fired applications, heat transfer surfaces have to be periodically cleaned (e.g. by soot-blowing), which results in peak particulate matter concentrations above 50 mg/Nm^3. Consequently, it is proposed to base the proposed AEL on a monthly average.

4.2.   LOW NO$_X$ BURNERS ON FIRED HEATERS AND BOILERS

The process characteristics of these technologies are described in more detail in Chapter 5 of this report which addresses Catalytic Crackers. There are specific aspects of SNCR technology when applied to heaters and boilers that can impact on the efficiency. Firstly operating temperatures for SNCR are relatively high so that residence time at the appropriate temperature may be a problem in some boilers. Secondly the ammonia/urea addition needs to be adjusted to the gas flow so that in heaters/boilers experiencing a fluctuating load and/or changes in feed gas quality abatement may be more difficult to control than in equal sized units operating under steady conditions.

4.2.1.   SNCR for heaters and boilers

4.2.1.1.   Current BREF

BREF paragraph 4.10.4.6 contains AEL ranges for the application of SNCR on heaters and boilers, whereas paragraph 4.23.3.2 contains similar information for waste gas treatment in general. Both paragraphs mention a NO$_x$ reduction efficiency between 40 and 70%.

Furthermore both paragraphs show AEL levels for heaters and boilers (BREF table 4.28) for different fuel types and one value (par. 4.23.3.2) for waste gas applications in general.

Paragraph 4.23.3.2 refers to a range for ammonia slip of 5-40 mg/Nm^3.

Finally, paragraph 4.10.4.6 (under the item 'Applicability') mentions that SNCR requires temperatures at above 650°C.

4.2.1.2.   Plant data

Datasets on 3 boilers show an emission reduction performance ranging between 25 and 40%. This is based on 3 datasets on dual liquid/gas firing.

ID	CEMS	Thermal Power	Fuel type	%N in liquid fuel	% liquid fuel / total fuel	Unabated NO_x emissions (mg/Nm^3 @ 3% O_2 dry gas)	SNCR efficiency (% NO_x abatement)	comments
SNCR 1	Y	98 MW	mixed liquid/gas	0,40-0,50	30-95	244-810	25-40	40% abatement only obtained for one specific boiler load. Accelerated corrosion observed even with ammonia slip < 5 ppm
SNCR 2	N	45 MW	mixed liquid/gas	0,34-0,45	80-95	667-877	25-30	ammonia slip > 15 ppm for 30% abatment
SNCR 3	N	45 MW	mixed liquid/gas	0,34-0,45	70-90	568-780	25-30	

4.2.1.3. Proposed amendments

Based on the above observations it is proposed to amend paragraphs 4.10.4.6 and 4.23.3.2 of the BREF to replace the range of 40-70% by 25-70% reduction efficiency for boilers and heaters. This reduction efficiency range is only applicable if inlet NO_x concentrations are above 200 mg/Nm^3, because even under optimal circumstances there is a lower limit to the technically achievable NO_x outlet concentration.

It is further proposed to delete the AEL ranges for emission concentration levels downstream of the SNCR application.

There is some inconsistency in the BREF with respect to the required temperature level for SNCR: par. 4.10.4.6 mentions 650°C, whereas par. 4.5.8.2 (referring to FCC applications) indicates a range of 800-900°C and par. 4.23.3.2 refers to a range of 800-1200°C.

US EPA mentions a range of 870-1090°C, which is consistent with practical observations. It is therefore proposed to change the required temperature range in paragraph 4.10.4.6 to 870-1090°C

Below this temperature window, the reaction kinetics become very slow and inefficient. Above, the NH_3 is oxidized into NO, which actually increases the stack, NO_x emissions.

The requirements for a high NO_x reduction efficiency include:

- Good mixing between the urea and the stream of combustion products,
- Adequate temperature window in the mixing region,
- Adequate residence time (at least 0.2 to 0.5 s in the region of injection)
- No impingement of the injected chemical against the furnace tubes.

Thus, application of the SNCR technique in existing furnaces and boilers requires well chosen injection locations and a mixing region with appropriate temperature and size to allow for sufficient NO reduction. In practice, this is very difficult to achieve as temperature profile in the boiler varies with boiler load.

Another limitation to SNCR is the emission of a small amount of unreacted NH_3 (ammonia slip) in the flue gas stream after the NO_x reduction. The ammonia slip is typically in the range from 5 to 20 ppm, with the higher values associated to higher NO_x reduction efficiencies. Moreover, for heaters burning sulphur containing fuels, the ammonia slip leads to formation of ammonium sulfates that tend to deposit further downstream on cold parts (tubes of furnace, convective section, boiler economizer). These deposits could lead to accelerated corrosion. This risk of ammonium sulfate deposition imposes to operate with a low ammonia slip, hence decreasing the efficiency of the NO_x reduction.

Furthermore it is proposed to include the comment that "applicability of SNCR to heaters and boilers is generally limited as there is not enough residence time at the required temperature level".

It is proposed to add a new AEL range to paragraph 5.2.10: 25-70% for the NO_x reduction efficiency of SNCR on boilers and heaters. This reduction efficiency range is only applicable to inlet NO_x concentrations above 200 mg/Nm^3 because, even under optimal circumstances, there is a lower limit to the technically achievable outlet concentration.

4.2.2. SCR on heaters and boilers

4.2.2.1. Current BREF

Both paragraph 4.10.4.7 (heaters and boilers) and 4.23.3.3 (general waste gas applications) contain an AEL range for NO_x reduction efficiency of 90-94% and 80-95% respectively.

Paragraph 4.23.3.3 (general waste gas applications) refers to an emission level of 10-20 mg/Nm^3 NO_x for gas firing and <100 mg/Nm^3 for heavy residue firing.

In paragraph 4.10.4.7 and Chapter 5.2, paragraph 10 (at 3 places in the text) it is mentioned that an ammonia slip level of 2-5 mg/Nm^3 is achievable and that this level increases with catalyst life. In Paragraph 4.23.3.3, referring to general flue gas treatment techniques, a range of <2-20 mg/Nm^3 is mentioned.

4.2.2.2. Plant data

The 2 datasets on SCR, one covering 1 mixed gas/oil fired heater and the other covering a common stack of 4 mixed gas/oil fired boilers show a level of 80-82% removal resulting in an outlet concentration between 90 and 120 mg/Nm^3 for inlet concentrations of 500-600 mg/Nm^3.

4.2.2.3. Proposed amendments

The BREF performance level referred to above indicating that SCR is capable of reducing NO_x by 90-94% in boiler and heater applications is not consistent with paragraph 4.23.3.3 which mentions a range of 80-95%.

Based on this comment and also on the observed plant data it is proposed to:

- Replace the range of 90-94% in paragraph 4.10.4.7 by 80-95%. Include this AEL also in paragraph 5.2.10. This reduction efficiency range is only applicable to inlet NO_x concentrations above a certain level because even under optimal circumstances there is a lower limit to the technically achievable outlet concentration. Data is only available for relatively high inlet concentrations (>500 mg/Nm^3) and tentatively we propose about 200 mg/Nm^3.

- It is further proposed to include a comment on applicability mentioning that for existing heaters and boilers the expected NO_x reduction performance depends on the amount of catalyst and on how the unit can be fitted into the existing flue gas duct systems. Include the same comment also in paragraph 5.2.10.

- As far as the ammonia slip level is concerned it is proposed to make the numbers consistent and realistic. Therefore it is proposed to include a range of 2-20 mg/Nm^3 in paragraphs 4.10.4.7, 4.23.3.3 and 5.2.10.

5. FLUIDISED CATALYTIC CRACKING UNITS

5.1. INTRODUCING CONCEPTS

The following general paragraphs apply to Fluidised Catalytic Cracking Unit (FCCU) operation related emissions. These general concepts are introduced here and referred to throughout this report. It is proposed that the below text and concepts should be included in the revised BREF document under section 4.5 to enable the context of the BREF to be better understood by the end user.

5.1.1. Function of the CO Boiler (COB) in a FCC

In this report three main types of FCCU modes are discussed:

- Partial burn units with a downstream CO Boiler (COB),
- Full burn units (or partial burn units) with a downstream auxiliary fired boiler,
- Full burn units without a downstream auxiliary fired boiler.

The distinction between partial burn and full burn units is described in section 5.2.1. It is important to distinguish between the different function of the COB versus the auxiliary fired boiler.

A CO Boiler (COB) used in conjunction with a partial burn unit has the primary function of controlling CO emissions by incinerating the CO exiting the regenerator to CO_2. Additional fuel is needed to ensure that the CO is burned and although the COB is usually equipped with heat recovery to produce steam the additional fuel supply to this type of COB is generally only the amount required for CO incineration rather than for steam generation per se although exceptions exist. In this report, this type of CO Boiler (primarily CO Incineration function) is simply referred to as a COB.

An auxiliary fired boiler can be used in conjunction with either a partial or a full burn FCC unit with the primary function being to produce steam. In the partial burn case the amount of fuel used is significantly higher than just the amount needed to incinerate CO to CO_2. In full burn units where the primary use of the COB has changed from CO incineration to steam production we will follow the convention of naming the boiler auxiliary fired COB. Generally a full burn unit with an auxiliary fired boiler will have been converted from a partial burn unit with a COB.

It is also important to distinguish the difference between a waste heat recovery boiler and a COB. A waste heat recovery boiler is used only to recover heat from the process via its heat exchange coils. This type of boiler is not fired, this being the main distinction which differentiates it from the COB. It should perhaps more properly be called a heat exchanger or waste heat boiler.

NO_x emissions from an auxiliary fired boiler (steam production) can be significantly higher than that from a COB (CO incineration). This is because of the higher fuel firing carried out in the auxiliary fired boiler and is especially the case when the fuel contains high amounts of fuel-bound nitrogen and/or ammonia. With LNB technology installed, AELs similar to those in other boilers may be achieved taking into account fuel nitrogen equivalences if boiler base design allows.

5.1.2. Impacts of processing residual feedstock in a FCCU

The following general comments can be made regarding FCC processing. In the EU region there is a growing trend towards processing more residual feedstock in FCCUs in response to increasing demand for road transport fuels and a decreasing demand for residual fuels. Residual feedstock properties include: higher content of coke precursors, higher levels of metals (i.e. Ni, V) and an increased content of sulphur, nitrogen and aromatics. These properties can result in the following environmental impacts.

Potential consequences of the high metals content include:

- A substantial increase in: catalyst addition rate and associated withdrawal (of equilibrium catalyst (ECAT) and potentially higher regenerator losses due to increased catalyst attrition (typically withdrawal losses will increase more significantly than regenerator losses).
- The formation of FeS (from the increased feed Fe content) over the equilibrium catalyst, which is then oxidized to SO_2 and SO_3 in the regenerator thus increasing flue gas SO_x content.
- Increasing NO_x emissions due to required antimony additions (see section 5.2). The antimony is used to passivate nickel to reduce the production of hydrogen.

Consequences of the increased feed sulphur content include:

- Higher coke sulphur and consequently higher SO_x emissions.

Consequences of increased feed nitrogen content include:

- Potentially increased production of NO_x precursor compounds: NH_3 and HCN which may or may not lead to increased NO_x emissions depending on the FCCU regenerator operations.

5.2. NO_X EMISSIONS FROM A CO BOILER (COB) AND FROM A FULL BURN REGENERATOR WITHOUT COB

5.2.1. Introduction and background information

Overall, the FCC Unit can be a significant source of NO_x emissions at a typical Refinery and a potential (small) source of N_2O which is a greenhouse gas. An explanation of the mechanisms by which NO_x is formed in combustion can be found in Chapter 4.

In a FCCU coke is deposited on the cracking catalyst and must be removed. This is done in the FCCU regenerator by combustion in a fluidized bed. The combustion air acts as the medium for fluidization of the catalyst particles. The combustion temperature level within an FCCU regenerator is typically too low for formation of thermal and prompt NO_x.

To understand the formation of NO_x in a FCC regenerator it is essential to distinguish between the two possible modes of operation:

- Full burn units have the objective of converting the coke to CO_2 and to have negligible CO in the regenerator flue gas. The main mechanism for the formation of FCCU NO_x is oxidation of nitrogen species in the feed which are transferred from the reactor into the regenerator via coke on catalyst (Fuel NO_x in the nomenclature of section 4). Multiple intermediate species are formed as the coke is burned, many of which are converted to N_2. However some are oxidized to NO_x. In general FCCU NO_x mainly consists of NO (in the order of >90% of total NO_x) the balance being NO_2. Furthermore low levels of N_2O could also be emitted.

- Partial burn units also have the objective of converting the coke to CO_2 but produce excess CO (typically in the range 3-7%v) in the regenerator flue gas which is subsequently converted to CO_2 in the COB. In partial burn units the main species contributing to NO_x emissions are predominantly the NO_x precursors (HCN, NH_3), which are formed under the higher excess CO process conditions in the regenerator. These species leave the regenerator and enter the COB where they are largely converted to NO_x.

A wide range of variables, to varying degrees, effect NO_x emissions from the FCCU. The presence of coke nitrogen is an essential source for FCC NO_x, however the majority of the coke nitrogen is converted to molecular nitrogen (N_2). Normal variations in feed nitrogen content do not usually affect NO_x emissions significantly. The parameters affecting NO_x emissions vary from partial to full burn regenerators due to the different mechanisms of NO_x formation and the varying N species in each burn scenario.

Key parameters, potentially affecting FCCU NO_x emissions in full burn mode are:

- Regenerator equipment configuration may result in uneven regenerator catalyst bed temperature and oxygen profiles and distribution or poor spent catalyst and / or air distribution. Typically more even distributions will result in lower NO_x emissions.
- The use of a Carbon Monoxide (CO) combustion promoter, historically containing platinum, can increase NO_x substantially. Raising the level of platinum (Pt) can further increase NO_x formation. New generation low NO_x (non-Pt) combustion Promoters may in some cases decrease NO_x and still keep afterburning of CO under control (see Section 5.6 for more information).
- Antimony additions, often used for high-metal feed applications (see section 5.2.3.2), have often been correlated with increased NO_x emissions.

Key parameters, potentially affecting FCCU NO_x emissions in partial burn mode are:

- Formation of NO_x precursor compounds (HCN and NH_3). A part of the coke nitrogen is converted to HCN and NH_3 depending upon the CO content. Operating conditions at higher excess CO usually favour the formation of these precursors which react to form NO_x and N_2 in the CO boiler downstream of the regenerator. As discussed above, some thermal NO_x can be generated in the CO boiler or fuel NO_x can be formed depending upon the nitrogen content of the supplemental fuel, the amount and type of fuel, the burner design and the operating conditions in the CO Boiler.

- The final stack NO_x emissions may be similar to or even higher than an equivalent full burn regenerator. It is typically higher than a full burn unit operating at low excess O_2 (<2%).

5.2.2. Current BREF associated emission ranges and limits

The Associated Emission ranges and Limits (AEL) for NO_x emissions from a COB (partial burn) and from a full burn regenerator without a COB that are given in the first version of the BREF are summarized as shown in **Table 5-1**.

Table 5-1 BREF Emission Limit Ranges for uncontrolled NO_x

Monitor & Control of O_2 >2% in Full Combustion units.	300-700 mg NOx/Nm^3 (chapter 4.5.1) [1] 300-600 mg NOx/Nm^3 (chapter 5.2.5) [2]
The use of a downstream COB with Partial Combustion.	100-500 mg NOx/Nm^3 (chapter 4.5.3)[2] 100-300 mg NOx/Nm^3 (chapter 5.2.5) [2]

[1] - Value attainable in continuous operation. Emissions values as half-hourly mean values.
[2] - corrected to 3% O_2 dry, emissions values as daily averages.

5.2.3. Discussion of BREF

5.2.3.1. Discussion of supporting real plant data

11 FCCU Datasets have been collected, as shown in **Table 5-2**.
2 are Full burn units without auxiliary firing boilers.
9 are Partial Burn Units with a CO Boiler.

Table 5-2 Summary of unabated NO_x emissions datasets

Dataset No	Type of Application	Observations
6	8 Partial burn units with COB.	• NO_x emissions at the exit to the COB range from 85 to 500 mg/Nm^3 for 7 of the units. • One unit with COB using supplementary fuel for enhanced steam production: NO_x emissions up to 800 mg/Nm^3 [CEM daily av.]
8	Partial burn unit with COB.	• NO_x emissions from the COB daily average 254 mg/Nm^3; hourly 95th percentile 345 mg/Nm^3 [CEM hourly av.]
9	Full burn unit without auxiliary fired boiler using Antimony catalyst.	• NO_x emissions at the exit from the regenerator daily average 567 mg/Nm^3; daily 95th percentile 989 mg/Nm^3. [CEM hourly av.] • Residual fuel application with antimony injections.
11	Full burn unit without auxiliary fired boiler.	• NO_x emissions at the exit from the regenerator daily average 86 mg/Nm^3; daily 95th percentile 188 mg/Nm^3. [CEM daily av.]

NOTE: Unless otherwise specified all NO_x emissions are corrected to 3% O_2.
Datasets collected by CONCAWE have been assigned anonymous numbers to respect confidentiality of member companies.

5.2.3.2. Conclusions derived from plant data

From the observations outlined in **Table 5-2** the following conclusions can be made regarding the BREF AELs:

- The chapter 4 and 5 AELs, as per **Table 5-1** are not met in every case, as illustrated by datasets 6 and 9. In the case of residual fuel applications where antinomy additions are required, dataset 9, NO_x emissions are significantly higher, up to 990 mg/Nm^3 (@ 3% O_2). In residual processing there is typically a lot of nickel in the feed. The nickel gets laid down on the catalyst and starts to catalyze dehydrogenation reactions hence producing molecular H_2 which increases the load on the wet gas compressor. This often leads to the wet gas compressor becoming the primary unit constraint, sometimes forcing a reduction in feed rate to cope with the low molecular weight fuel gas. Antimony is commonly used as an additive on residual feed applications to suppress the production of H_2 from the action of nickel and hence allows the unit to operate at full feed rate. A common side-effect of Antimony additions can be an increase in NO_x emissions, in some cases of up to 4 fold magnitude.

- The Chapter 5 upper AEL range of 300 mg/Nm^3 for partial burn units with a COB is not achievable for some of the datasets shown in **Table 5-2**.

- The Chapter 4 upper AEL range of 500 mg/Nm^3 for partial burn units with a COB is not achievable in the case of the COB being utilized for Refinery steam production – in particular for units with a high supplementary fuel consumption and firing heavy residue in the COB (see dataset 6 where NO_x emissions are up to 800 mg/Nm^3).

5.2.4. Proposed amendments to BREF

Based on the conclusions described above the following amendments are proposed:

- Paragraph 4.5.1 & 4.5.3

  1. Add the following comment about the consistency of FCC performance: "The NO_x emission from a FCC unit can increased over time as the quality of air catalyst mixing in the regenerator deteriorates as a result of wear. For example, internal mechanical damage could occur towards the end run of the unit and this could significantly increase all unit emissions (NO_x, SO_x and PM)" (paragraphs 4.5.1 & 4.5.3).

  2. Add the following comments (paragraph 5.2.5) about processing residual feedstock:
     "The processing of residual feedstock can have specific environmental impacts, including an increase in NO_x emissions, as described in section 5.1.2 of this report. Hence in the case of a unit running predominantly residual feedstock through the FCC the current BREF AELs may not be met for the following reasons:

     o Potential consequences of the high metals content include: increased NO_x emissions due to antimony additions.
     o Consequences of increased feed nitrogen content include: increased production of NO or of NO_x precursors such as NH_3 and HCN".

3. All emission performance ranges to be based on daily (or longer) average values (for reference in the US the averaging periods are 7-day for rolling short term and 365 days for long term average). The current, tight half-hourly average described in Chapter 4.5.1 is inconsistent with the averaging time stated in Chapter 5 for the same BAT AEL range. Furthermore, it is extremely difficult to meet half-hourly plant limits in case of variations of operating conditions or abnormal processing events.

- Paragraph 4.5.1

  1. Make an exception to the current AEL range of 300-700 mg/Nm^3 for full burn applications with antimony additions. Amend upper AEL to 1000 mg/Nm^3 in case of injection of antimony (residual feedstock cracking), which is very likely to significantly increase NO$_x$. While it is noted that such levels of NO$_x$ emissions are considered very high it is proposed to document this as an upper range for unabated NO$_x$ emissions from a FCCU (paragraph 4.5.1).

  2. Add the following comment under cross-media effects: "In full burn mode, when excess O$_2$ is reduced to around 0.5%, NO$_x$ production is dramatically reduced; however, SO$_x$ production is typically increased. A possible explanation of the increased SO$_x$ is that with less O$_2$ the coke is not completely burned off the catalyst. The catalyst then generates more coke, and increased coke production correlates to larger SO$_x$ production."

- Paragraph 4.5.3

  1. Amend the current upper AEL range for partial burn data from the current 100-500 mg NO$_x$/Nm^3 (chapter 4.5.3) to 100-800 mg/Nm^3 to account for higher emissions resulting from COB use for steam production (high supplementary fuel consumption).

- Paragraph 5.2.5

  1. Align the AEL range for full burn units with the AEL proposed for paragraph 4.5.1 (300-700 mg/Nm^3) and include a separate AEL range for residual feedstock cases with antimony injection (300-1000 mg/Nm^3).

  2. Align the AEL range for partial burn units to the AEL proposed for paragraph 4.5.3 (100-800 mg/Nm^3) and document the distinction between a COB being used as an incinerator versus a steam boiler, as described in section 5.1.1 of this report.

5.3. CO EMISSIONS FROM A COB AND FROM A FULL BURN REGENERATOR WITHOUT A COB

5.3.1. Introduction and background information

In the FCCU unit relatively high concentrations of carbon monoxide can be produced during regeneration of the catalyst and it is typically converted to carbon dioxide either in the regenerator (full burn or total combustion) or further downstream in a carbon monoxide boiler (COB) (partial combustion). The CO emissions from FCC units are dependent on: regenerator temperatures, combustion

promoter level and type, size of regenerator and mixing conditions and the conditions under which the regenerator is operating. In some full burn regenerators CO emissions are controlled by maintaining a certain excess O_2 in the flue gas.

5.3.2. Discussion of BREF

5.3.2.1. Current BREF associated emission ranges and limits

The current BREF provides values for CO emissions from FCCUs utilizing COB (partial burn) and O_2 control (full burn) in varying modes of operation, as summarized in **Table 5-3**.

Table 5-3 BREF CO Emission AELs for full burn FCCU and partial FCCU with COB

Monitor and Control O_2 >2% for Full Combustion units.	35-250 mg CO/Nm^3 (chapter 4.5.1) [1] 50-100 mg CO/Nm^3 (chapter 5.2.5) [2]
Partial Combustion (controlled to 3% O_2 and standard conditions) with downstream COB.	50-400 mg CO/Nm^3 (chapter 4.5.3) [2] 50-100 mg CO/Nm^3 (chapter 5.2.5) [2]

All values attainable in continuous operation.
[1] – corrected to 3% O_2 dry, half-hourly averages.
[2] – corrected to 3% O_2 dry, daily average, standard conditions.

5.3.2.2. Discussion of supporting real plant data

One dataset has been collected showing CO emissions on a full burn unit with the use of regenerator excess O_2 control only.

Table 5-4 Summary of unabated CO emissions

Dataset No	Type of Application	Observations
3	Full burn unit without COB.	• CO emissions daily average 398 mg/Nm^3; daily 95th percentile 831 mg/Nm^3 [CEM 8hrly av.] • O_2 <2%

NOTE: Unless otherwise specified all CO emissions are corrected to 3% O_2.

5.3.2.3. Conclusions derived from plant data

From the observations outlined in **Table 5-4** the following conclusions can be made regarding the BREF AELs:

The Chapter 4 upper AEL of 250 mg/Nm^3 is not met for the full burn application where O_2 is less than 2% (see dataset 3).

5.3.3. Proposed amendments to BREF

Based on the conclusions described above the following amendments are proposed:

• Paragraph 4.5.1

1. Add comment that the AEL range of 35-250 mg/Nm^3 is strictly only met if the O$_2$ is above 2%. In cases where the unit is running at O$_2$ <2% these AELs may not be met due to significantly higher CO emissions at low O$_2$ levels.

2. Amend the value for full burn units of 35-250 mg CO/Nm^3 (chapter 4.5.1) to a daily average to make consistent with reminder of BREF AELs and Chapter 5 of the BREF.

- Paragraph 5.2.5

1. Amend AEL range in Chapter 5.5 to be equivalent to Chapters 4.5.1 and 4.5.3 for the full burn control with O$_2$ and also for partial burn units with COB control.

5.4. FCCU SO$_X$ REDUCING ADDITIVES (SRA)

5.4.1. Introduction and background information

Sulphur dioxide in the regenerator off-gas of a FCC unit can be reduced by using a SO$_x$ reducing catalyst which allows part of the SO$_x$ produced in the regenerator to be transferred back to the reactor, where it is converted to hydrogen sulphide (H$_2$S). This is taken off with the product stream where it can be further treated in the Sulphur Recovery units.

The SO$_x$ Reducing Additives (SRAs) reduce regenerator SO$_x$ emissions via the following mechanism:

a) Catalytic oxidation of SO$_2$ to SO$_3$ in the regenerator.
b) Chemisorption on the additive of SO$_3$ produced in the regenerator to form a sulphate.
c) Additive circulates to the FCC reactor, where it is converted to H$_2$S in the reducing environment of the reactor and leaves the reactor in the product gas stream.

SRAs are added to the regenerator, in a similar way to fresh catalyst. It should be noted that at additive loading rates greater than 10–15% of Fresh Catalyst Addition (FCA), the dilution of cracking catalyst with additives may adversely affect FCCU yields.

The ability of an additive to reduce SO$_x$ emissions is typically measured using a 'pick-up factor' (PUF), which is the mass (kilograms) of SO$_x$ removed per unit mass (kilogram) of additive present in the catalyst inventory. Partial burn regenerators typically observe PUF factors that are significantly lower than those in full burn units. Furthermore, some partial burn units have seen no reduction of SO$_x$ at all with the use of additives. The performance of SRAs is very unit specific for both partial and full burn units.

5.4.2. Discussion of BREF

5.4.2.1. Current BREF associated emission ranges and limits

The current BREF provides emission reduction efficiencies associated with the use of SRAs on catalytic crackers in varying modes of operation as summarized in **Table 5-5**.

Table 5-5 BREF Emission Reduction Efficiencies for SO_x Reducing additives

Full Combustion (controlled to 3% O_2)	20-60% emission reduction (chapter 4.5.10.1) [1]
Partial Combustion (controlled to 3% O_2)	Up to 30% emission reduction (chapter 4.5.10.1) [1]
Typical Downstream Effluent SO_2 Concentration	1300-3000 mg/Nm^3 (chapter 4.5.10.1) [1] [2]

[1]- corrected to 3% O_2 dry.
[2]- based on input concentration of 4250 mg/Nm^3 @ 3% O_2, feedstock sulphur approx. 2.5%.

Also, according to the current BREF document, known disadvantages/ operational constraints of SO_x Reducing additives (SRAs) are:

- SRAs are more efficient in full burn mode.
- Potential poorer yield of products from FCC unit (at high additive loading rates >10% of fresh catalyst addition) due to dilution of the base catalyst, and depending upon the circulation of the SRA in the circulating catalyst inventory.
- Reduced FCC unit operating flexibility.
- Since sulphur is shifted from air emissions to H_2S in the reactor products, the increased H_2S must be removed to meet product quality specifications. The H_2S handling facilities may limit SRA usage due to possible bottlenecks from the increased H_2S load. Energy usage will also increase.
- Potential fouling affecting unit reliability (e.g. cyclones, expander blades).
- Potential increased attrition rate and hence increased losses of catalyst resulting in increased PM emissions.

5.4.2.2. Discussion of supporting real plant data

Two FCCU datasets, showing SRA performances, have been collected, both for full burn units as summarized in **Table 5-6**.

Table 5-6 Summary of SO_x Reducing additives datasets

Dataset No	Type of Application	Observations
1	Full burn unit, 0.7% O_2, max 6% of catalyst inventory.	• 3 different additive brands tested. • On average 60% reduction achieved.
2	Full burn unit, 0.6-0.7% O_2, max 8% of catalyst inventory. 0.1-0.7% sulphur in feed (%wt).	• SO_2 outlet emissions achieved 10-350 kg/day based on inlet SO_2 of 150-450 kg/day [CEM daily averages]. • Daily reduction average: 66%; daily 95th percentile reduction 86%. • Higher range of SO_2 reduction achieved when running low S feed.

Note: Unless otherwise specified all emission values are corrected to 3% O_2 dry.

5.4.2.3. **Conclusions derived from plant data**

- The range provided in the BREF for reduction efficiency associated with SRAs, 20-60% for full burn, is consistent with the emissions shown in the above datasets. Reduction efficiency is highly dependent on the sulphur content of the feedstock. Given that a substantial part of European refineries operate their FCCs at feedstock sulphur content varying over a broad range, high reduction values are difficult to maintain consistently.

Other issues to note from operational experience include:

- The typical upper limit of SRA addition rate is about 10% of the Fresh Catalyst addition (FCA) as industry experience shows. Above this addition rate yield impacts are likely.

- When defining AELs for SO_2 emissions and performance of SRAs, the averaging period is very important since there can be a wide variation of parameters which affect regenerator SO_x, such as feedstock sulphur content and type of feed sulphur.

5.4.3. **Proposed amendments to BREF**

- Paragraph 4.5.10.1

    1. Add the following comment regarding factors affecting SO_x reduction efficiency. "The outlet SO_x emission concentration achieved with the use of SRAs is highly dependent on SO_x inlet concentrations, amount of SRA that can be used and the unit operating mode".

    2. Add the following comment under the applicability section: "The typical upper limit of SRA addition rate is about 10% of the Fresh Catalyst addition (FCA). Industry experience shows that above this addition rate, negative unit yield impacts are likely".

    3. Amend the following sentence in the BREF text as it is not accurate: "SO_x Reducing additive is more efficient in full burn mode. However, full burn implies more SO_x and NO_x formation than partial combustion mode". SO_x emission is similar for full and partial burn operation, whereas NO_x leaving the regenerator in partial burn mode is usually lower compared to full burn, but combustion of the NO_x precursors in the COB can result in higher stack NO_x emissions for partial burn.

    4. Add the following paragraph regarding averaging period for emissions; "When defining AELs for SO_2 emissions and performance of SRAs, the averaging period is an important factor since there can be a wide variation of parameters which affect the SO_x, such as feedstock sulphur content and type of feed sulphur. The proposal is for a monthly average or at the least a 7 day rolling average to account for the variation in the feed sulphur properties".

    5. Add the following remarks to paragraphs 4.5.10.1 and 5.2.5 regarding the cross media effects and operational issues associated with SRAs:

- The potential increase of attrition results in more fine particles and hence potential increased PM emissions.

- Conditions favourable to increasing SRA efficiency may lead to an increase in uncontrolled NO_x emissions.

5.5. FCCU NO_X REDUCING ADDITIVES (NRA)

5.5.1. Introduction and background information

NO_x Reduction additives fall into two principal types: (a) Non-Platinum based Combustion Promoters (discussed separately under section 5.6) and (b) NO_x reducing additives per se. NO_x reducing additives (NRAs) catalyze nitrogen intermediates to form molecular nitrogen and catalyze the reduction of NO_x to nitrogen. The success of NRAs is unit dependent as its effectiveness depends on the mixing dynamics of fluidized spent catalyst and combustion air. There may also be some observable yield effects, with certain units reporting an increased production of hydrogen.

Within the past several years, the industry has used NRAs to try to lower NO_x emissions from the FCCU regenerator. Main issues reported are:

- Swings in the regenerator flue gas oxygen concentration and temperature during the initial loading of additive.
- Increase in hydrogen production in some cases.
- Interference with SO_x reducing additive performance, in some instances reducing its effectiveness.
- Unit specific NO_x response: in some cases no change is observed in the outlet NO_x concentration and in other cases some NO_x reduction is observed.

5.5.2. Discussion of BREF

5.5.2.1. Current BREF associated emission ranges and limits

The current BREF does not specify NO_x Reducing additives as a Best Available Technique; therefore there are no AELs available for comparison and for discussion here.

5.5.2.2. Discussion of plant data

Two FCCU Datasets showing NO_x reducing additive performance were available, both for full burn units, as well as results from a US benchmarking survey, summarized in **Table 5-7**.

Table 5-7 Summary of NO$_x$ Reducing additives datasets

Dataset No	Type of Application	Observations
5	Full burn unit with auxiliary fired boiler.	• Trialled 4 NO$_x$ Reducing Additives in combination with 3 COPs (2 non-Pt and one Pt). • NO$_x$ reducing additives used in conjunction with low NO$_x$ COPs (non-Pt) did not have significant effect on reducing NO$_x$ emissions.
19	Full burn unit without COB.	• Unabated NO$_x$ emissions ranging from 70 to 225 mg/Nm^3 were reduced down to 21-164 mg/Nm^3. The average efficiency achieved was a 60% reduction in NO$_x$. [~1 year trial]. • Significant spikes in NO$_x$ emissions during the trial were attributed to the use of promoted ECAT[#] or Pt combustion promoter, which typically increases NO$_x$ emissions.
19	US Benchmarking Plot showing summary of 27 trials in the US (both full and partial burn units).	• The US industry benchmarking average is at 26% NO$_x$ reduction for full burn units (with performance ranging from 0 to 80% reduction) and 0% for partial burn units. • Based on >25 unit trials in total. • Several cases where 0% reduction was achieved on full burn units.

NOTE: Unless otherwise specified all NO$_x$ emissions are corrected to 3% O$_2$.
- ECAT: Equilibrium catalyst.

5.5.2.3.   Conclusions derived from plant data

• NRAs have not been proven effective in all full burn unit cases, with their performance being highly variable and unit specific, hence not easily predictable.

• Different brands/types of NRAs have shown varying performance (see dataset 5).

• NRAs are not effective at all on partial burn units; this being mainly attributed to NO$_x$ precursors being the dominant species in the partial burn mode of operation (NRAs are not designed to target these species).

Additional issues that have been noted from operational experience include:

• An increase in hydrogen production in some cases.
• Regenerator flue gas oxygen concentration and temperature swings when the NRA is initially loaded. (Note: typically a lot of material is initially added over a short timeframe to build a certain percentage in the inventory). NRAs are typically loaded to 0.25 wt% in about 1 week, if loaded at higher percentages problems with oxygen concentration and temperature control could occur.
• Interference with SO$_x$ reducing additive performance (if used in conjunction with NRAs).
• Possible increase in coke and gas yields with copper-based NRAs Using an addition rate greater than 1.5% by weight of catalyst make up can result in an increase in SO$_2$ emissions for copper based NRAs. This is because the copper based NRA can pick up sulphur in the reactor where it is transferred to the

regenerator. The typical addition rate of NRAs is 0.5 to 1.5% by weight of catalyst makeup.

Additionally, although not a problem as such with NRAs, situations causing a temporary increase in NO_x concentrations may overwhelm the capability of the NRA. Examples include temporary overdosing of platinum based combustion promoters, disturbance of catalyst air mixing in the regenerator fluidised bed.

5.5.3.   Proposed amendments to BREF

Add NO_x Reducing Additives (NRAs) to chapter 4.0 as a technique that has moved beyond "emerging" but is not yet fully proven. NRAs are a technology with a lot of potential but, because some applications have not shown a good response for poorly understood reasons, it cannot yet be considered a fully proven technology for all full burn applications. The datasets collected show a high variability in performance, being very unit dependent and in some cases mo reduction is achieved. Setting BREF AELs is not possible at this early stage. The reduction performance has a wide range from ineffective up to 60% reduction in NO_x concentrations.

Add the comment: "For partial burn units there are currently no effective NRAs available". This is due to the fact that in partial burn different species of nitrogen are involved in NO_x formation, i.e. NO_x precursors HCN and NH_3, which are converted to NO_x in the COB.

5.6.   FCCU LOW NO_X COMBUSTION PROMOTER (COP) ADDITIVES

5.6.1.   Introduction and background information

NO_x reduction additives fall into two principal types: Non-Pt based Combustion Promoters (COP) and the NO_x reduction additives discussed in Section 5.5.

Historically, industry used Pt-based COP in those FCCU regenerators where afterburning is an operational problem. Afterburning is the oxidation of CO to CO_2 in the dilute phase and in the cyclones and can cause temperature excursions above the equipment design limits of the regenerator internals. The combustion promoter catalyzes the rapid combustion of CO in the catalyst bed of the regenerator, however, the platinum present in the promoter can also increase the formation of NO_x.

Where needed, combustion promoters are applied in two ways: premixed with the catalyst (both for initial bed charging and for makeup feed) or by separate batch addition. If NO_x concentrations need to be reduced then the first control option is to reduce the platinum load in the bed, either through minimising the addition rate or reducing the platinum content of the additive. However, as afterburning needs to be kept under control, this option can be limited. As a second option non platinum-based COPs can be used. However these non-platinum based COPs could be less effective in controlling afterburning. Industry experience has shown that in order to achieve comparable afterburning control additive dosage has been higher (by up to 8 times) than a conventional platinum promoter. Unfortunately, in cases where higher quantities of non-platinum COP are used, NO_x can actually increase.

5.6.2. Discussion of BREF

5.6.2.1. Current BREF associated emission ranges and limits

The current BREF does not provide specific AELs for use of Low NO_x combustion promoters.

5.6.2.2. Discussion of supporting real plant data

There are 2 FCCU Datasets showing low NO_x COP performance and both are for full burn units, as shown in **Table 5-8**.

Table 5-8   Summary of Low NO_x Combustion Promoter datasets

Dataset No	Type of Application	Observations
5	Full burn unit with auxiliary fired boiler.	• Trialled 2 Low NO_x COP's. One controlled CO effectively and reduced NO_x; the other did not control CO. • NO_x controlled to <70 mg/Nm^3 from inlet emissions of 175-260 mg/Nm^3
13	Full burn unit with auxiliary fired boiler.	• Emissions associated with Pt COP 820-1025 g/Nm^3 NO_x. • Switch to Low NOx COP resulted in emissions of 410-720 mg/Nm^3 NO_x [CEM hourly averages] [1]

[1]- Following one month transition period.
Unless otherwise stated all emission values are corrected to 3% O_2 dry.

Additionally it was noted that several units in the US (both full and partial burn) have shown no improvement at all in NO_x emissions with the implementation of the Low NO_x COP.

5.6.2.3. Conclusions derived from plant data

The conclusions derived from the above datasets are:

The performance of different types of Low NO_x COP is variable, with some effectively controlling CO as well as reducing NO_x and others not at all efficient for their intended purpose of CO control.

The datasets indicate that in some cases the use of a low NO_x COP can effectively control afterburning and at a lower NO_x level compared to conventional Pt-based COP.

Additionally the following observations have been made in relation to the applicability of Low NO_x COP:

• The use of low NO_x COP can require higher addition rates, up to 8 times greater than for platinum based combustion promoters.
• Low- NO_x COP can result in unacceptable increase in afterburning or in CO emissions in some cases.

- In some cases of high addition rate the use of Low NO_x COP has failed to reduce NO_x altogether.

5.6.3. Proposed amendments to BREF

Following are suggested amendments to the BREF:

- Section 4.5

    1. Add a section on Low NO_x (non-Pt) COP as a technique which has the potential to control CO and afterburning but at a lower NO_x level compared to the use of Pt-based COPs. It is only applicable in full burn units.

    2. Add the following paragraph on optimising the use of Combustion Promoters.: "If NO_x concentrations need to be reduced then the first control option is to reduce the platinum load in the bed, either through minimising the addition rate or reducing the platinum content of the additive. However, as afterburning needs to be kept under control, this option can be limited."

    3. Include the following applicability notes on Low NO_x COP:

        - Low NO_x COP is an option for NO_x reduction in systems already using a platinum based COP to control afterburning.
        - Low NO_x COP is not applicable at all for partial burn FCCs.
        - To achieve an acceptable level of afterburning by using low NO_x COP it may be necessary to significantly increase the dosage rate compared to conventional platinum based COPs and at high dosage rates there may be a NO_x penalty.

5.7. FCCU SELECTIVE NON-CATALYTIC REDUCTION (SNCR)

5.7.1. Introduction and background information

A Selective Non-Catalytic Cracking Reduction (SNCR) process uses either ammonia or urea injected into the hot flue gas at a temperature high enough to allow chemical reduction of NO_x to nitrogen without a need for a catalyst. The required temperature range is 870–1090°C. SNCR can therefore be applied in partial burn units with a CO boiler and full burn units with an auxiliary boiler provided that there is sufficient residence time in the system. However, in a full burn unit not having an auxiliary boiler the operating temperatures are always too low for SNCR. There is another potential route to NO_x reduction in such systems. Adding hydrogen to the regenerator overhead gas stream lowers the operating temperature window required for SNCR reactions. If there is sufficient residence time available, ammonia injected into the overhead line or into a downstream boiler/furnace may be effective. This technique only works for ammonia based systems.

There are two types of SNCR - ammonia based and urea based. Urea based systems require extra residence time because the urea is injected as a liquid and therefore the urea must first vaporize and dissociate before the NO_x reduction reactions can start.

It should be noted that NH_3 reacts primarily with NO and much more slowly with NO_2. Because the NO_2 content of FCC or combustion NO_x can be up to 10% this imposes a fundamental limit on the overall NO_x removal efficiency of SNCR systems operating within the necessary constraints of fixed residence time and minimisation of ammonia slip.

For SNCR the percentage reduction efficiency is the most relevant performance parameter as the mixing efficiency between NH_3 and NO and the residence time at the required temperature range for reaction are in most cases the controlling factors regardless of the inlet concentration. The ultimate NO_x outlet concentration is set by the thermodynamic equilibrium. The lowest achievable concentration is typically around 80 mg/Nm^3 for the typical operating temperature range for SNCR applied to FCCU and taking account of the low conversion of NO_2.

5.7.2.   Discussion of BREF

5.7.2.1.   Current BREF associated emission ranges and limits

The AELs for Selective Non-Catalytic Reduction as per the BREF are summarised in **Table 5-9**.

Table 5-9 BREF Emission Reduction Efficiencies for SNCR's

Outlet NO_x concentrations achieved with SNCR (partial and full burn units)	<200-400 mg/Nm^3 (Section 4.5.8.2) [1]
Technology Reduction Efficiency	40-80% (Section 4.5.8.2) 60-70% (Section 5.2.5)
Ammonia slip	2-5 mg/Nm^3 (Section 5.2.5)

[1] - depending on the nitrogen content of the feedstock, corrected to 3% O_2 dry, daily averages.

5.7.2.2.   Discussion of supporting real plant data

3 Datasets are available on SNCR applications, as summarised in **Table 5-10**.

Table 5-10 Summary SNCR datasets

Dataset No	Type of Application	Observations
12	Full burn unit with an auxiliary fired boiler.	The average reduction efficiency was 23%. The inlet NO_x range was 123-410 mg/Nm^3 [CEM daily av.] [1] The average ammonia slip was <15 mg/Nm^3.
14	Full burn unit with an auxiliary fired boiler for refinery steam production (Regenerator Overhead Line Injection).	The average reduction efficiency was 50%. The 95th percentile reduction efficiency was 81%. The inlet NO_x range was 90-530 mg/Nm^3. The outlet NO_x range was 50-180 mg/Nm^3 [CEM daily av.] [1] Ammonia slip hourly average was 8 mg/Nm^3; 95th percentile 15 mg/Nm^3.
16	Partial burn unit with a COB.	SNCR upstream of a wet gas scrubber (WGS). The SNCR average efficiency was 67% on an hourly basis. The 95th percentile reduction was 78% on an hourly basis. The average inlet NO_x concentration was 318 mg/Nm^3 and the 95th percentile was 420 mg/Nm^3 both on an hourly basis. The average outlet NO_x concentration (downstream of the WGS and the SNCR unit) was 99 mg/Nm^3 and the 95th percentile was 165 mg/Nm^3 both determined by CEM on an hourly average. [1] The hourly average ammonia slip was 10 mg/Nm^3.

[1] – corrected to 3% O_2 dry.

5.7.2.3. Conclusions derived from plant data

The following conclusion can be made from the above datasets.

- The reduction efficiency of the SNCR technology is unit dependent which is reflected in the spread of results. In one case the average NO_x reduction efficiency was 23% (dataset 12), and two datasets were below the current BREF lower BAT AEL range of 60% NO_x reduction [Section 5.2.5].

- The hourly averaged ammonia slip ranged between 8 and 15 mg/Nm^3. This is outside the upper range of the BREF AEL of 2-5 mg/Nm^3 [Section 5.2.5].

Comments on Cross media effects

- One issue that is of particular concern with SNCR applications in FCCUs is the potential for an associated increase in CO emissions. At the lower end of the SNCR operating temperature range ammonia can inhibit CO oxidation. Therefore, if the COB temperature is low, CO emission

concentrations could increase and this should be a consideration when considering the suitability of SNCR in retrofit applications.

- Another issue is the potential increase in N_2O, a greenhouse gas (GHG) which can be formed in the SNCR process, especially if urea is used. The magnitude of the increase seems to be related to the NH_3/NO_x molar ratio and the operating temperature. The applications using H_2 may result in higher N_2O concentrations.

5.7.3. Proposed amendments to BREF

- Chapter 4.5.8.2 & Chapter 5

  1. Amend the current Emission Reduction Efficiency for SNCR from 40-80% to 20-70% to better reflect the actual performance range of the technology as shown in the datasets provided.

  2. It is proposed to amend the ammonia slip range to 2-20 mg/Nm^3 to be consistent with our observations and considering that no data is given in section 4.5.8.2 of the BREF. This is the narrower than the range quoted for applications of SNCR in waste gas treatment in the BREF section 4.23.3.2. There is a relationship between the achievable NO_x removal efficiency and ammonia slip: a higher NO_x removal performance requires more ammonia resulting in a higher ammonia slip.

- Chapter 4.5.8.2

Include the following comments under the relevant headings in this section:

Applicability

  1. The reduction efficiency is dependent on: CO Boiler residence time at the required temperature range for SNCR, CO Boiler temperature profile, inlet temperature, and allowable NH_3 Slip. The latter is the only parameter which can be controlled by the operator. The other factors are fixed characteristics of the installation (paragraph 4.5.8.2).

     Add the following comment to paragraph 4.5.8.2: "During specific non-routine operational episodes, e.g. when the FCCU is in operation but the COB is shutdown, emissions could differ significantly from the performance during normal operation. Such special operational episodes are not covered by the AEL range."

  2. SNCR applications are most effective in the flue gas temperature window of 870-1090°C. The effective temperature window can be extended down to about 700°C by addition of hydrogen but this application is limited to the use of ammonia as the SNCR reagent. The process of vaporization and dissociation of urea precludes the use of hydrogen with urea-based SNCR.

  3. SNCR cannot be applied to COBs which have a flue gas temperature above 1090°C and therefore SNCR is not BAT for this type of equipment.

4. The BREF also states in paragraph 4.5.8.2 that this technology "is applicable in partial combustion FCCs with CO boiler and retrofitting in existing CO boilers is relatively simple". It is proposed to replace this sentence by the following comments: "As the reduction efficiency is very dependent on the COB configuration and residence time, application of SNCR in retrofits of FCCs with a CO boiler may not result in optimal performance. It can also be applicable to full combustion units either: applied in the regenerator overhead line using hydrogen addition or in an auxiliary fired boiler. Space requirements are mainly related to NH_3 storage".

Cross-media effects

- One issue that is of particular concern with SNCR applications in FCCUs is the potential for an associated increase in CO emissions. At the lower end of the SNCR operating temperature range ammonia can inhibit CO oxidation. Therefore, if the COB temperature is low, CO emission concentrations could increase and this should be a consideration when considering the suitability of SNCR in retrofit applications.

- Another issue is the potential increase in N_2O, a greenhouse gas (GHG) which can be formed in the SNCR process, especially if urea is used. The magnitude of the increase seems to be related to the NH_3/NO_x molar ratio and the operating temperature. The applications using H_2 may result in higher N_2O concentrations.

5.8.   FCCU SELECTIVE CATALYTIC REDUCTION (SCR)

5.8.1.   Introduction and background information

In the Selective Catalytic Reduction (SCR) process NO_x is reduced to nitrogen and water by a chemical reaction with ammonia over a separate fixed catalyst bed. This is situated downstream of the FCCU regenerator. The use of a catalyst allows for the NO_x reduction reaction to take place at lower temperatures compared to SNCR. A typical temperature range is 300-400°C. As for SNCR processes the reduction reaction rate of NO is faster then for NO_2. Although usually only less than 10% of the FCC NO_x is present as NO_2, this limits the NO_x reduction potential to some extent of systems operating within the necessary constraints of fixed residence time and minimisation of ammonia slip.

As FCCU regenerator flue gas contains particulates, primarily catalyst fines, particulate deposition on the SCR catalyst beds may cause pressure build up and plugging. The catalyst bed is cleared using sonic horns or soot-blowers whilst on-stream.

There is an open debate around whether SCR's should be installed upstream or downstream of the particulate control technology. If the SCR is downstream of the PM control equipment this can minimise plugging of the catalyst beds. However, it is still necessary to clean the catalyst bed and this may lead to periodic episodes of increased PM emissions during the cleaning operation. If the SCR is upstream of the PM control equipment then the plugging problem could be more severe.

In addition to mechanical blockage by catalyst fines, SCR performance can deteriorate over time due to catalyst deactivation or plugging by several routes

(metals, hydrocarbons, ammonium bisulphate salts, etc). This can impact the achievable run-time between turnarounds.

5.8.2. Discussion of BREF

5.8.2.1. Current BREF associated emission ranges and limits

The AELs for Selective Catalytic Reduction as per the BREF are summarised in **Table 5-11**.

Table 5-11 BREF Emission Reduction Efficiencies for SCR's

Inlet NO_x concentrations into an SCR (partial and full burn units)	200-2000 mg/Nm^3 (chapter 4.5.8.1) [1]
Outlet NO_x concentrations achieved with SCR (partial and full burn units)	30-250 mg/Nm^3 (chapter 4.5.8.1) [1]
Technology Reduction Efficiency	85-90% emission reduction (chapter 4.5.8.1 & chapter 5.2.5) [1] Ammonia slip 2-5 mg/Nm^3 (chapter 5.2.5) [1]

[1] – corrected to 3% O_2 dry, daily averages.

5.8.2.2. Discussion of supporting plant data

3 datasets have been collected for SCR applications, all full burn units, as summarised in **Table 5-12**.

Table 5-12 Summary SCR datasets

Dataset No	Type of Application	Observations
10	Full burn unit with auxiliary fired boiler.	SCR Reduction efficiency daily average 88% NO_x reduction. Inlet NO_x range 36-244 mg/Nm^3 [CEM daily av.] [1] Outlet NO_x range 2-26 mg/Nm^3 [CEM daily av.] [1] Frequency of shutdowns ~ 4 years.
11	Full burn unit.	SCR efficiency for NO_x daily average 91% reduction. Inlet NO_x range 25-111 mg/Nm^3 [CEM daily av.] [1] Outlet NO_x range 3-12.8 mg/Nm^3 [CEM daily av.] [1] Frequency of shutdowns ~ 7 to 17 months.
15	Full burn unit with auxiliary fired boiler.	SCR Reduction efficiency for NO_x averaging at 85%. Lower efficiency (<70%) towards end of unit run-life (due to pressure build-up). Inlet NO_x range 44-251 mg/Nm^3 [CEM daily av.] [1] Outlet NO_x average 2.6-54 mg/Nm^3 [CEM daily av.] [1] Run time between shutdowns ~ 4 years.

[1] – corrected to 3% O_2 dry.
Ranges are calculated by taking the 5th to the 95th percentile of the complete dataset.

5.8.2.3. Conclusions derived from plant data

The outlet NO_x range is within the range as specified in the BREF of 30-250 mg/Nm^3.

The daily average achieved SCR reduction efficiency is between 85-92% which is consistent with the range specified in the BREF in Section 4.8.1.

The SCR will require a periodic shutdown for cleaning and/or catalyst replacement. The frequency of shutdown can be highly variable, from 7 months to 4 years depending on the severity of plugging.

5.8.3. Proposed amendments to BREF

Paragraph 4.5.8.

It is proposed to amend the comment in the BREF paragraph 4.5.8.1 which states "run time of SCR unit can be up to 6 years". Experience from sites, as illustrated in the datasets above, shows that the shutdown frequency for cleaning is highly dependent on the unit configuration and can be as low as every 7 months. Fouling by salts or catalyst fines causes a build up of pressure drop over the catalyst bed. The pressure drop at which the SCR must shutdown is very FCCU specific. Furthermore, the rate of catalyst fouling can be affected by the location of the SCR in the process scheme (i.e. it may be less prone to plugging if installed downstream of an ESP or other particulate control device). The above mentioned AEL is only applicable to normal operations, excluding shutdown periods for cleaning.

It is proposed to change the range for ammonia slip in paragraph 4.5.8.1 from <2-10 mg/Nm^3 to 2-20 mg/Nm^3, consistent with our proposed amendment for the application of SCR on fired heaters and boilers and with the BREF section 4.23.3.3 on waste gas treatment.

It is proposed that the following comment be included in paragraph 4.5.8.1: "The application of a SCR could reduce the potential for energy recovery using expander turbines, which is BAT for energy recovery. The operation of a SCR unit increases the pressure drop over the regenerator overhead circuit and is also prone to a build-up of pressure drop over time, thereby limiting the available operating window for a turbine expander, particularly in existing facilities with fixed pressure profiles".

It is proposed to amend the comment in paragraph 4.5.8.1 of the BREF which states that "retro-fit application is highly applicable". It is proposed to include the following comment: "SCR requires a temperature range of typically 300-400°C. This can complicate retrofit applications where the auxiliary fired boiler/COB circuits or the waste heat boiler system regenerator flue gas system may have to be modified to establish the required inlet temperature for SCR."

5.9. FCCU SCRUBBERS

5.9.1. Introduction and background information

Scrubbers are designed to remove primarily SO_2 and particulate matter from flue gas streams. This report focused on absorption and/or chemisorption in a dispersed liquid. Additional stages can also target NO_x but are not addressed in this report.

Wet gas scrubbers remove air pollutants by absorption/reaction (chemisorption) either with a sorbent or reagent slurry, or by absorption into a liquid solvent. There are many types of scrubber configurations (orifice, venturi, filter-bed, mechanical, spray and packed towers). Data presented here is for venturi scrubbers.

In venturi scrubbers the flue gas stream is contacted with the scrubbing sorbent by turbulent mixing within a venturi throat, where the scrubbing liquid is atomized and particulates are removed with the atomised liquor.

Venturi Scrubbers require less plot space compared to other wet scrubber types. Two types of are commercially available:

- Jet Ejector Venturi Scrubbers. Absorption liquid is sprayed into the flue gas stream at the inlet of the venturi above the 'throat'. Gas and liquid then pass through the throat under conditions of high turbulence.

- High Energy Venturi Scrubbers. These use the kinetic energy of the flue gas to break the absorption liquid into droplets. This technology requires more gas pressure drop but it has higher removal efficiency for small particulates compared to Jet Ejector Venturi Scrubbers, in particular for PM10 and PM2.5, typically being able to remove down to PM2.

5.9.2. Discussion of BREF

5.9.2.1. Current BREF associated emission ranges and limits

The current BREF AELs for Wet Gas Scrubbers are shown below in **Table 5-13**. These are generic values (including venturi scrubbers) but additional information on venturi scrubbers is given in the BREF section 4.5.10.3.

Table 5-13 First version BREF AELs for Wet Gas Scrubbers

Emission	AELs	Section
Outlet PM Concentration (WGSs)	10-40 mg/Nm^3 <10-35 mg/Nm^3 <30-50 mg/Nm^3	5.2.5.2[1] 4.5.10.2 4.23.4.4
Outlet SO$_2$ Concentration (WGSs)	10-400 mg/Nm^3 10-350 mg/Nm^3	4.5.10.2 5.2.5.2
PM % Reduction Efficiency (Venturi Scrubbers)	93%	4.5.10.3
SO$_2$ % Reduction Efficiency (Venturi Scrubbers)	93%	4.5.10.3

5.9.2.2. Discussion of plant data

Datasets showing the performance of Venturi type wet scrubbers are summarised in **Table 5-14**. The PM data refer to the total particulate mass measured directly at the scrubber outlet at seven facilities in the USA.

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[1] This is the BAT range for FCCU emissions allowing abatement by any technology and is not specific to WGS.

Table 5-14 Summary of Venturi WGS's datasets

Dataset No	Type of Application	Observations
7a	Partial burn unit with a COB	Outlet PM emissions range 35-60 mg/Nm^3 average 47 mg/Nm^3 [1]
7b	Partial burn unit with a COB	Outlet PM emissions range 39-50 mg/Nm^3 average 46 mg/Nm^3 [1]
7c	Full burn unit	Outlet PM emissions range 48-109 mg/Nm^3 average 74 mg/Nm^3 [1]
7d	Full burn unit	Outlet PM emissions average 56 mg/Nm^3 [1]
7f	Partial burn unit with a COB	Outlet PM emissions range 43-61 mg/Nm^3 average 56 mg/Nm^3 [1]
17	Partial burn unit with a COB	Outlet emissions at daily average of 61 mg/Nm^3 SO_2 [CEM hourly av.] Inlet SO_2 average of 425 mg/Nm^3. An average of 90% reduction in SO_2 emissions. Jet Ejector Venturi type scrubber.
18	Partial burn unit with COB	Outlet emissions daily average 125 mg/Nm^3; 95th percentile 160 mg/Nm^3 SO_2 [CEM hourly]. Inlet SO_2 emission estimated at >1800 mg/Nm^3. 93% removal efficiency for both SO_2 and PM. Jet Ejector Venturi type scrubber.

[1] – Based on discontinuous spot measurements.
Unless otherwise specified all values are corrected to 3% O_2 dry basis.

5.9.2.3.   Conclusions derived from plant data

Where SO_2 inlet concentrations are available we calculate that reduction efficiency is in the range 90-93% compared with the BREF AEL single value of 93%. The daily average SO_2 outlet emissions are within the BREF range for generic WGS

The lower range of the BREF AEL for outlet SO_2 concentration from a WGS of 10 mg/Nm^3 (4.5.10.2) is very low compared with both the data and typical US Consent Decree concentrations expresses as both short term (120 mg/Nm^3 at 3% O_2) and long term (60 mg/Nm^3) averages.

The SO_2 outlet concentration of Dataset 18 reflects that the unit now operates at a higher SO_2 inlet load compared to its original design.

The PM concentrations reported here (total PM basis) range from 46 to 74 mg/Nm^3 compared to the range of <10-35 mg/Nm^3 cited in the BREF section 4.5.10.2 and the range <30-50 mg/Nm^3 cited in the BREF section 4.23.4.4. It should be noted that the measurement method used here may include condensation residues (salts etc,) which could lead to higher PM mass loadings than might be obtained by other methods.

In addition to the datasets the following operational issues have been collected from the refining sites and industry experts:

- In the BREF paragraph 4.5.10.2 it is stated that "a suitably designed wet scrubbing process will normally provide an effective removal efficiency of both SO_2/SO_3 and particulates". However, wet scrubbers have a low removal efficiency of SO_3. Typical SO_3 removal values are 25 to 50%; this is much lower than removal efficiency of SO_2 and particulates. In addition, particulate removal efficiency depends on the type of wet scrubber.

- In the BREF paragraph 4.5.10.2 it is stated that "wet scrubbing processes generate low pressure drop, operate at low temperature and do not create solid deposition problems". Operational experience has found that deposition problems can occur on a time-scale of five years. The amount of deposition depends on the inlet catalyst and SO_2 load to the scrubber, the quality of the make-up water, the operating pH of the scrubber and level of purge applied to the scrubbing slurry. The deposits essentially comprise catalyst dust that settles at low points and on mist eliminators and hardness deposits such salts of calcium etc that precipitate as the operating pH is increased to achieve high SO_2 removal efficiency.

- In the BREF paragraph 4.5.10.2 and 4.5.10.3 it is stated that "These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide etc.". This statement could be misleading. Venturi scrubbers remove particulates and SO_2 simultaneously. Venturi scrubbers convert the SO_2 to salts such as sodium sulphite, sodium bisulphite and sodium sulphate. They are designed with a small purge to control the level of salts and particulates in the circulating slurry. Jet ejector and high energy venturi scrubbers typically have low sulphur trioxide emissions, unlike packed or spray towers. Any wet scrubber regardless of the type that has circulating slurry is designed with a purge.

- In the BREF paragraph 4.5.10.3 it is stated that "venturi scrubbers are widely applied for the treatment of small flows". Approximately 50% of the wet scrubbers on FCC units are venturi scrubbers and typically these are not small flows.

5.9.3. Proposed amendments to BREF

1. It is proposed to replace the parameter 'SO_x' (BREF paragraph 4.5.10.2, table 4.10) by 'SO_2'.

2. It is proposed to remove the reduction efficiencies for PM, SO_2 and NO_x from table 4.10 in the BREF paragraph 4.5.10.2 as it is not the most suitable performance parameter of a WGS.

3. It is proposed to amend the current AEL range for SO_2 (BREF paragraph 4.5.10.2, table 4.10) of 10-400 mg/Nm^3 outlet SO_2 emissions to 60-400 mg/Nm^3.

4. It is proposed to amend the current AEL for PM (BREF paragraph 4.5.10.2, table 4.10) of <10-35 mg/Nm^3 to 30-60 mg/Nm^3 PM outlet emissions.

5. It is proposed to remove the 93% removal efficiency for SO_2 and PM as currently stated in the BREF paragraph 4.5.10.3 and to refer to table 4.10 of BREF section 4.5.10.2.

Furthermore it is proposed to include the following operational comments on operational data, applicability and cross-media effects:

1. In the BREF paragraph 4.5.10.2 it is stated that "a suitably designed wet scrubbing process will normally provide an effective removal efficiency of both SO_2/SO_3 and particulates". It is proposed to add the following comment "However, wet scrubbers have a low removal efficiency of SO_3. Typical SO_3 removal values are 25 to 50%; this is much lower than removal efficiency of SO_2 and particulates. In addition, particulate removal efficiency depends on the type of wet scrubber"

2. It is proposed to amend the cross-media effect stated in the BREF paragraph 4.5.10.2 as "wet scrubbing processes generate low pressure drop, operate at low temperature and do not create solid deposition problems". It is proposed to include the following comment: "The performance of Wet Gas Scrubbers can be affected by deposition problems occurring in the course of a five year run. The amount of deposition depends on the inlet catalyst and SO_2 load to the scrubber, the quality of the make-up water, the operating pH of the scrubber and level of purge applied to the scrubbing slurry. The deposits essentially comprise catalyst dust that settles at low points and on mist eliminators and hardness deposits such salts of calcium etc that precipitate as the operating pH is increased to achieve high SO_2 removal efficiency."

3. It is proposed to remove the following statement from the BREF paragraphs 4.5.10.2 and 4.5.10.3: "These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide etc." .

4. It is proposed to remove the following statement from the BREF paragraph 4.5.10.3: "Venturi scrubbers are widely applied for the treatment of small flows".

5.10.   THIRD STAGE BACKFLOW FILTERS

5.10.1.   Introduction and background information

Mechanical filters are used to trap particles as they pass through the system. Third stage backflow filters have recently been used to reduce FCCU particulate emissions. These filters act as a third stage of particulate removal following for example a set of cyclones. These filters are comprised of a sintered porous metal or ceramic filter element that is designed for surface filtration. The filter medium provides a surface on which a cake of particles continues to build up until a predetermined pressure drop is reached. A reverse flow of clean gas (blowback) is then introduced to remove the filter cake from the elements. These solids can be returned directly to the FCC process for reuse or placed in a collection unit for disposal or further treatment.

5.10.2.   Discussion of BREF

5.10.2.1.   Current BREF associated emission ranges and limits

The current BREF does not currently discuss third-stage backflow filters as a BAT for FCCUs.

5.10.2.2.   Discussion of supporting plant data

There is currently an application of a third-stage backflow filter on an FCC unit in the Southern Hemisphere which has a typical daily flow of 2100 tons. No performance data is available; however the following comments related to its applicability have been collated from operating experience:

Applicability

- The third stage backflow filters have very limited applicability for FCCs as they have only been proven on small flue gas lines; flow of 2100 tons/day, and not on the large scale of a typical FCC unit.
- The filter can remain in operation during FCCU upset conditions, start-up and shut-down conditions, which allows for control of emissions during these events.
- Safety in process conditions is also a concern with full flow filters. A potential blockage could lead to over-pressurizing of the regenerator system and it may be necessary to have inbuilt safety devices (e.g. bypasses).

5.10.3.   Proposed amendments to BREF

Add third-stage backflow filters as an emerging BAT in the BREF document. State that the technology has limitations in applicability related to the size of the unit, and it has so far only been proven on one small scale FCCU outside of Europe.

5.11.   ELECTROSTATIC PRECIPITATORS (ESP- PARTICULATES)

5.11.1.   Introduction and background information

Particulate emissions from FCC units are mainly catalyst and additives fines that contain varying levels of metal compounds depending upon specific unit operations.

Electro-static precipitators (ESP) are installed on many FCCUs worldwide, and can provide > 90% particulate capture, including capture of some sub 10 micron particulates. Collection efficiency can be improved in certain cases by the injection of ammonia upstream, although this may lead to increased ammonia emissions. Typically the ESP will be de-energized on FCCU start-up to avoid the risk of introducing hydrocarbon to an ignition source and creating a potential explosion hazard. As a consequence, during start-up particulate emissions will be greater than during normal operations. There are two implications for recommending AEL values. Either the start-up conditions should be excluded and the AELs refer to normal operations or the averaging period for the AELs be defined to be sufficiently long that that start up transient is accounted for, for example the BREF AEL might be defined as a monthly average value.

5.11.2. Discussion of BREF

5.11.2.1. Current BREF associated emission ranges and limits

The AELs for Electrostatic Precipitators as per the BREF are summarised in **Table 5-15**.

Table 5-15 BREF Emission Reduction Efficiencies for ESPs

Emissions Levels associated with ESPs	10-<50 mg/Nm^3 particulate matter in flue gas, excluding soot-blowing. (Section 4.5.9.2) [1]
Technology Reduction Efficiency	>99.8% (section 4.5.9.2)

[1] –This level is based on daily averaged continuous monitoring, excluding soot blowing

Additionally the BREF states the following:

Because these systems recover the fine particulates (mainly catalyst) coming from the FCCU, the refinery may need extra facilities to manage the fine particulates recovered. ESPs also consume electricity and will increase the energy demand of the FCCU.

5.11.2.2. Discussion of supporting plant data

2 datasets show the performance of ESPs on FCCUs, as summarised in **Table 5-16.**

Table 5-16 Summary of ESPs datasets

Dataset No	Type of Application	Observations
4	Stoichiometric full burn unit without a COB	• ESP Outlet PM Emissions average at 32 mg/Nm^3 (48 mg/Nm^3: 95th percentile). [CEM daily av.] • Estimated Reduction 93%. [1]
8	Partial burn unit with COB	• ESP Outlet PM Emissions average at 25 mg/Nm^3 (47 mg/Nm^3: 95th percentile). [CEM hourly av.] • Estimated Reduction 94%. [1]

Note: 95th percentile values are shown here to illustrate peaks in emissions occur for <5% of the time.
[1] – Emission reduction percentage calculated using upper value of 800 mg/Nm^3 as the inlet PM levels – taken from the unabated PM AEL of 350-800 mg/Nm^3 (as per Section 4.5.10.2 of the current BREF).

5.11.2.3. Conclusions derived from plant data

• The above datasets are consistent with the BREF AEL range of 10-50 mg/Nm^3 having 95th percentile hourly and daily averaged values below 50 mg/Nm^3. However, no measurements demonstrated that concentrations less than 25 mg/Nm^3 could be achieved on a sustained basis.

Additionally the following operational comments were collected from sites and FCC experts:

- To achieve the BREF lower AEL of 10 mg/Nm^3 requires a residence time greater than 30 seconds. This requires the ESP to be significantly larger than current units.

- In the BREF paragraph 4.5.9.2 it is stated that "ESP efficiency is not dependent on particle size". ESP collection effectiveness is a function of the particle size. The smaller the particle the more difficult it is to capture and to capture it requires a larger size of ESP and more energy.

- In the BREF paragraph 4.5.9.2 it is stated that ESP performance will degrade from start to the end of the run. Since minimal maintenance can be done to the ESP without an outage, degradation in performance is expected and recognised.

- In the BREF paragraph 4.5.9.2 it is stated that "particulate emissions from the FCC can be reduced to 1.1-2.3 kg/h". This sentence is meaningless without providing a context of unit size and throughput.

5.11.3.   Proposed amendments to BREF

Paragraph 4.5.9.2

1. Amend the averaging time for the BREF AEL range to be based on a monthly average to account for start-up and for operational peaks (occurring at <5% of the time).

2. Remove the emission technology efficiency AEL of >99.8% from paragraph 4.5.9.2 of the BREF as this is not a suitable measure of the performance of the ESP (paragraph 4.5.9.2).

3. Add the following comment on applicability: "An ESP must be closed down during FCCU during start-up and shut-down for essential safety reasons. BREF AELs for particulate emissions from FCCUs equipped with an ESP are therefore not applicable during these times" (paragraph 4.5.9.2).

Add the following comments and changes to the BREF paragraph 4.5.9.2.

1. Add the following paragraphs under the cross media effects: "There is a risk of an explosion in the event of a combustible mixture passing through an electrically charged ESP. Industry experience shows that two types of fires or explosions have been observed in ESPs, causing extensive damage. The first type is a fire in the dust collected on the ESP collecting plates or hoppers (carbon being the combustible material). The second type of fire occurs when a flammable mixture of gases (typically CO or hydrocarbon) explodes [7]. The most likely condition for a flammable gas cloud to enter an ESP attached to a FCCU is during unit restart or shutdown or as a consequence of unplanned unit conditions.

   Adequate operating procedures are required to mitigate this real risk. A very effective risk mitigation measure consists in a start-up or shut-down

sequence of the FCC unit without energizing the ESP, leaving it electrically isolated. In such procedure the ESP is not energized until the flue gas it receives is fully combusted, by either the regenerator or the CO boiler. As a consequence of this safety-required operation higher emissions of particulates will occur during start-up operations".

2. Add the following comment under applicability: "A residence time of greater than 30 seconds is needed to achieve the BREF lower AEL of 10 mg/Nm^3 greater than 30 seconds. This requires an ESP of a significantly larger size than current units".

3. Remove the following text in the BREF which states that "ESP efficiency is not dependent on particle size" (paragraph 4.5.9.2).

4. Add the following comment under applicability: "ESP performance will degrade from start to the end of the run. Since minimal maintenance can be done to the ESP without an outage, degradation in performance is expected" (paragraph 4.5.9.2).

5. Remove the following comment 'particulate emissions from the FCC can be reduced to 1.1-2.3 kg/h' (paragraph 4.5.9.2).

5.12. THIRD STAGE CYCLONE TECHNOLOGY

New improved cyclone technology, like Third-Stage Separators (TSS), is a common choice of clean-up device for particulates (BREF section 4.5.9.1) and as an aid to energy efficiency. The first attempts at power recovery from FCCU regenerator flue gas were unsuccessful because the expander blade lives were limited to a few weeks. It was found that particles 10 micron and larger were particularly harmful to the blades. Third stage separators were introduced to protect power recovery expander turbines from particulate damage. A TSS is a set of conventional cyclones, fitted externally to the regenerator but operating on the same principle as the regenerator internal first and second cyclones. These are high-velocity devices and recovered catalyst is returned to a dust hopper.

TSS separation performance varies considerably, mainly depending on the Particle Size Distribution (PSD) of the regenerator catalyst fines and the performance of the regenerator cyclones. Under normal unit operating conditions, the overall TSS efficiency is influenced by the following factors:

- Particle size distribution
- Concentrations of solids in the gas and its particle-density
- Cyclone geometry details
- Vapour flow rate, density and viscosity
- Mechanical condition of the cyclones (roundness, wall-roughness, leaks etc)

5.12.1. Current BREF associated emission ranges and limits

Table 5.17 BREF emission reduction efficiencies for 3rd stage cyclones, section 4.5.9.1

Inlet TSS	400-1000 mg/Nm^3
Outlet TSS	100-400 mg/Nm^3
Reduction efficiencies	30-90%

Table 5.18 Summary of datasets on 3rd stage cyclones

Based on 4 datasets	Inlet TSS mg/Nm^3	Outlet TSS mg/Nm^3
	165	24
	146	45
	Not measured	42
	Not measured	35

At 3 O_2 on dry basis

Table 5.19 Proposed additions to BREF

Inlet TSS	100-400 mg/Nm^3
Outlet TSS	50-400 mg/Nm^3, can be <50 depending on the inlet particle distribution and load.
Reduction efficiencies for loading <400 mg/Nm^3	>75% provided particle size distribution with median (by mass) >5 μm

At 3% O_2 on dry basis. Note that the lower limit of 50 mg/Nm^3 is the minimum level guaranteed by the technology supplier contingent upon the inlet particle size distribution.

5.12.2. Achieved environmental benefits

By reducing the particulate emission, the metal emissions are reduced. Depending on the above factors, 3rd stage cyclones with swirl tubes are generally efficient at removing small particles with a 50% cut point of about 2.5 microns and near capture for particles sized greater than 10 micron.

5.12.2.1. Cross-media effects

Catalyst fines recovered are considered as waste.

5.12.2.2. Operational data

A TSS generates a pressure drop in the flue gas stream. Good performance and reliability in many FCCs has been demonstrated.

Applicability

Applicable to any FCC.

5.12.3. Economics

Economics of disposal of the fine catalyst is around EUR 120-300 per tonne, including transportation.

51

5.12.4. Driving force for implementation

To improve control of emission of particulates.

5.12.5. Example plants

Many FFC units are operating with these systems.

6. AMINE TREATING

6.1. INTRODUCTION AND DESCRIPTON

Refinery fuel gas is an essential internal fuel for use in boilers and heaters but has variable composition and needs some pretreatment before use. In an amine treatment unit a stream intended for use as refinery fuel gas is contacted with a solvent to absorb H_2S. The desulphurised fuel gas can then be used in the refinery. The solvent is then regenerated, releasing H_2S which is sent to a sulphur recovery unit (SRU).

Refinery fuel gas is usually a blend from several sources, some originating from amine treating, while others (like PSA off gas from hydrogen purification of a hydro cracker) are already low in or free of sulphur and routed directly to the fuel gas system. Some sites vaporise LPG or import natural gas to provide the required fuel gas. In addition the amine treated fuel gases might have been treated in different units under different conditions and due to that differ in H_2S content.

There are many factors affecting the performance of an amine treatment unit but the main ones are the applied pressure, the solvent regeneration effectiveness and the operating temperature. The higher the pressure the lower the residual H_2S concentration in the fuel gas that can be obtained. Similarly the residual H_2S and CO_2 concentration in the solvent leaving the regenerator (depending on number of stripping trays, reboiler duty, stripping steam flow, etc.) affects the absorption efficiency.

Based on equilibrium data a window of achievable scrubber outlet H_2S was derived for a range of typical scrubber operating pressures and temperatures. As shown in **Table 6-1** this range was 2–220 mg/Nm^3 of H_2S in the cleaned gas for pressures ranging from 50 to 3.5 bara (higher pressures give better recovery) for temperatures between 35 to 50°C. The gas temperature is not dependent on pressure and can vary in this range.

The lowest concentrations can only be achieved in high pressure units and so this may require major modifications or replacement of older units. Note that fuel gas may contain sulphur in other forms than H_2S, for example, as mercaptans (originating from thermal cracking processes) and COS (mainly originating from FCC units). Mercaptans are not removed by amine treating and non-refining applications such as natural gas treating may require after-treatment steps. COS is difficult to remove.

Table 6-1 Typical H_2S content in fuel gas for a range of amine scrubber operating pressures

Amine Scrubber pressure, bara	Ranges for H_2S in fuel gas, mg/Nm^3
50	2-15
20	4-40
3.5	20-220

6.2. DISCUSSION OF BREF

6.2.1. Current BREF associated emission ranges and limits

The BAT Associated Emission Limits (AEL) in the current BREF of H_2S in fuel gas after Amine treating can be summarized as follow:

Table 6-2 BREF amine treated fuel gas H_2S ranges

BREF paragraph	System pressure in bar	H_2S concentration	
		mg/Nm^3	ppmv
2.10	All	<100	<65
2.10	20	20-30	13-20
4.23.5.1	All	20-200	13-130
4.23.5.1	3.5	80-140	52-91
4.23.5.1	20	20	13
5.2 (10) (23)	All	20-150	13-98

Table 6-3 BREF AEL SO_2 ranges for amine treated fuel gas firing

BREF paragraph	SO_2 range in mg/Nm^3 (dry, 3%V O_2)
5.2 (10)	5-20

6.2.2. Real plant data

Two sets of real plant data are available. One set concerns plant data of a 50 bar amine scrubber, the other of a 20 bar system. The H_2S concentration was continuously measured over the first three months of 2008 and recorded as daily averaged values. The daily average values are given in **Figure 6-1**.

Figure 6-1 Daily average fuel gas H_2S concentration after amine scrubbing
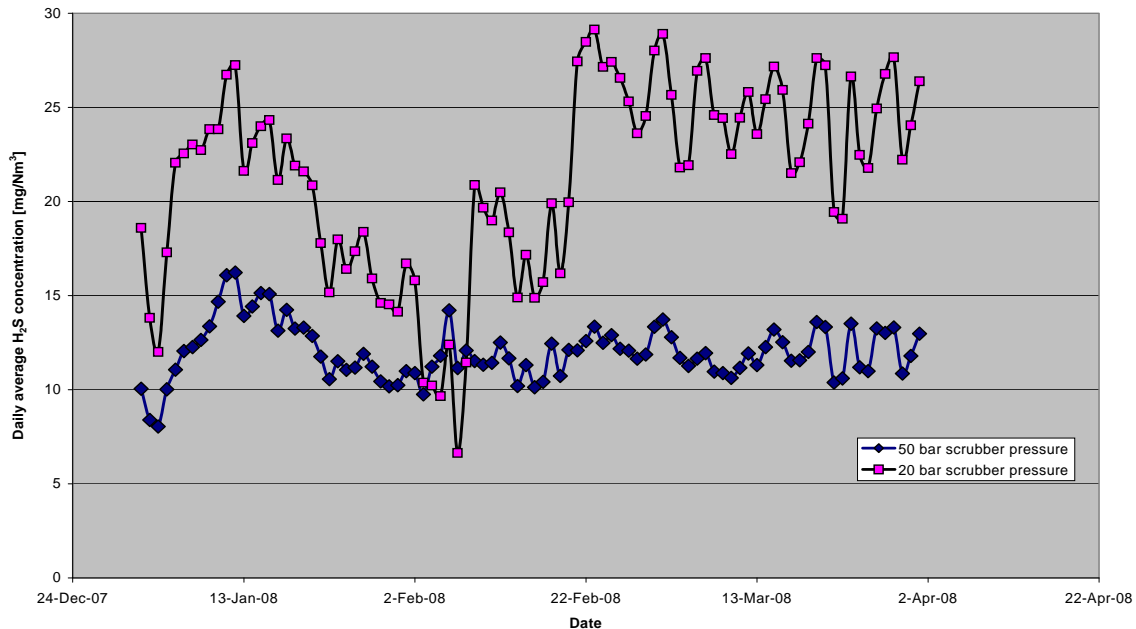
For the 20 bar system the H_2S concentration is <30 mg/Nm^3. For the 50 bar system this value is 17 mg/Nm^3. These are consistent with the calculated ranges shown in **Table 6-1**.

Based on **Table 6-1** the current BREF values correspond broadly to the middle of the operating range as it varies with temperature (noting that other sensitivities have not been tested) so we propose the following ranges:

Amine Scrubber pressure, bara	Proposed ranges for H_2S in fuel gas, mg/Nm^3
50	2-15
20	4-40
3.5	20-220

6.2.3. Achievable flue gas SO_2 concentration by amine treated fuel gas firing

The SO_2 concentration resulting from firing fuel gas treated in an amine scrubber is affected by the fuel gas H_2 content because emission concentrations are expressed on a dry basis. For a given fuel gas H_2S content the SO_2 concentration in the flue gas increases as the fuel gas H_2 content increases. This is shown in **Figure 6-2** for a fuel gas H_2S content equal to the proposed upper BREF range (220 mg/Nm^3). Based on this graph it is proposed to increase the upper BAT range for SO_2 from 20 to 35 mg/Nm^3. This proposed upper level covers a wide range fuel gas H_2 content (up to 45% vol). As the upper BAT range for H_2S corresponds to an amine scrubber pressure of 3.5 bara, it is clear that for a lower scrubber pressure the proposed upper BREF range of 35 mg/Nm^3 cannot be met at high fuel gas H_2 content.

Figure 6-2 SO$_2$ as a function of fuel gas H$_2$ content for upper BREF range
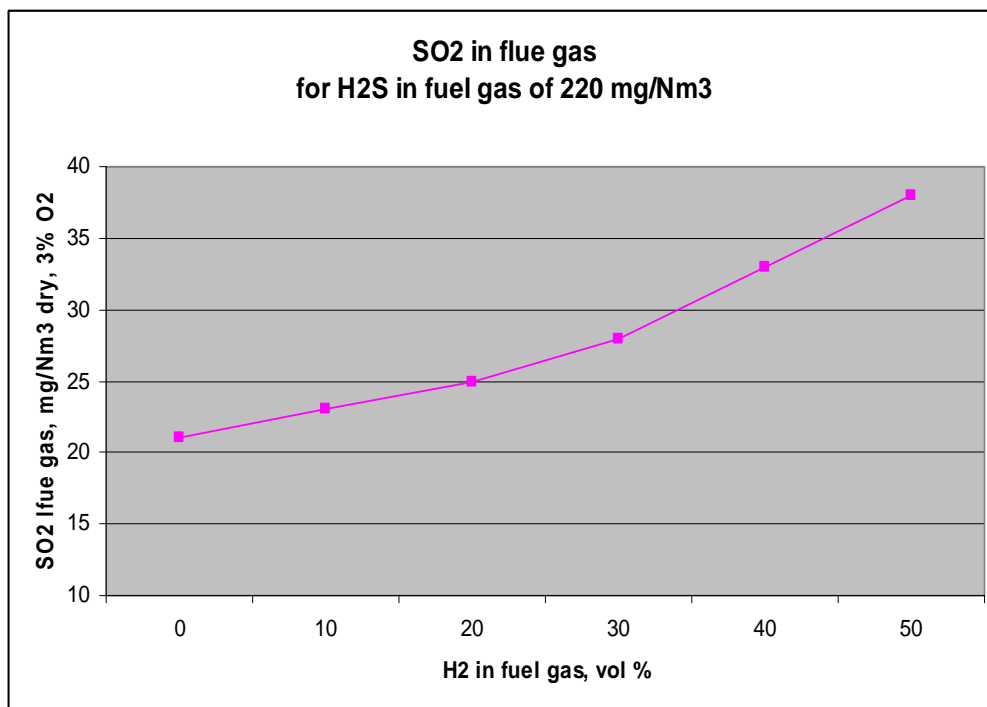
6.3. PROPOSED AMENDMENTS

1. Replace the current performance ranges in BREF paragraphs 2.10, 4.23.5.1 and the current AEL range in paragraphs 5.2.10 and 5.2.23 by the table below:

Amine Scrubber pressure, bara	Proposed ranges for H$_2$S in fuel gas, mg/Nm^3
50	2-15
20	4-40
3.5	20-220

2. Increase the upper BAT AEL range for SO$_2$ from gas firing applications from 20 mg/Nm^3 to 35 mg/Nm^3, dry @ 3% O$_2$ (par. 5.2.10).

3. Include a note that the proposed upper range of 35 mg/Nm^3 for SO$_2$ cannot be met for applications at a scrubber operating pressure lower than 3.5 bara and a fuel gas H$_2$ content above 45%.

4. Include a note that fuel gas may contain sulphur in other forms than H$_2$S, for example, as mercaptans (originating from thermal cracking processes) and COS (mainly originating from FCC units) Mercaptans are not removed by amine treating and non-refining applications such as natural gas treating may require after-treatment steps. COS is difficult to remove.

7. SULPHUR RECOVERY UNITS

7.1. OBJECTIVES

On request of CONCAWE, Sulphur Experts Inc. carried out an evaluation of sulphur recovery techniques in 2008 [6]. The prime purpose of this study was to collect real plant performance data for Claus plants and various Tail Gas Clean Up Units to establish a sound basis for an evaluation of the current information contained in the Refining BREF, and more specifically regarding performance levels and AELs for the overall sulphur recovery percentage and the mechanical availability of Sulphur Recovery Units (SRUs).

This chapter summarizes the results of the study done by Sulphur Experts and documents some proposed amendments to the current Refining BREF.

7.2. BRIEF DESCRIPTION OF SRU TECHNOLOGIES

In this chapter the term 'Sulphur Recovery Unit (SRU)' refers to process units or a combination of process units designed to convert H_2S into a liquid sulphur product.

This is achieved by either a stand alone Claus process or a combination of a Claus process followed by a Tail Gas Clean-Up (TGCU) unit for enhanced sulphur recovery. Such combination is also denominated SRU in this chapter.

SRUs typically treat concentrated H_2S streams from amine treating units but, in addition, can also treat streams originating from other refinery sources such as sour water stripper overhead gas streams. The latter type of stream typically contains mixtures of H_2S and ammonia. It should be noted that in some cases H_2S rich streams from amine treatment also contain some ammonia (typically in the order of a few %) and smaller amounts of CO_2 and hydrocarbons.

Claus units most commonly consist of 2 converter stages but some units consist of 3 converter stages for enhanced sulphur recovery. These two types are denominated 'Claus-2' and 'Claus-3' respectively.

TGCUs can be split up in the following 3 categories, according to the type of process being used:

- *Sub-dewpoint technologies*: these processes extend the sulphur recovery capability of the conventional two or three staged Claus plant by processing the Claus tail gas over a bed of standard Claus catalyst at a sub-dewpoint temperature. The most commonly employed sub-dewpoint processes used in industry today are: CBA, Maxisulf, MCRC, Sulfreen, Clinsulf. Another commercial process based on the sub-dewpoint concept is the Clauspol process in which the sub-dewpoint process takes place in a non-volatile liquid organic solvent instead of over a fixed bed catalyst.

- *Catalytic direct Oxidation technology:* this process employs a direct and selective oxidation reaction of H_2S directly to elemental sulphur over a proprietary catalyst. The most commonly used application is the Superclaus process which is always employed downstream of a conventional Claus unit. An enhanced version of the original Superclaus

process is the Euroclaus process which is intended to hydrolyse SO_2 in the Claus tail gas to H_2S prior to being processed in the oxidation reactor.

- *Amine based technology :* this technology was developed by Shell and most commonly involves 3 fundamental process steps,
  - o Conversion of all Claus tail gas sulphur species to H_2S via catalytic hydrogenation/hydrolysis.
  - o Cooling and removal of water from the process gas.
  - o Selective removal of H_2S from the process gas in an amine treating unit for recycling back to the Claus unit.
  - o Most commonly used applications include SCOT, BSR-MDEA, RAR, Sulften, Flexsorb SE.

7.3.   SUMMARY OF CURRENT BREF INFORMATION AND AELS

Paragraphs 4.23.5.2.1 and 4.23.5.2.2 of the BREF summarize the 'expected overall sulphur recovery yield ' for a number of SRU techniques, as per **Table 7-1**.

Table 7-1 BREF AELs for SRUs

	Process	Expected Sulphur Recovery yield, % (as daily average)
Claus unit	Claus 2 stage	94-96
	Claus 3 stage	97-98
Tail Gas Clean Up Units (1)	Superclaus	98.66
	Sulfreen	99.42
	Beavon	99-99.9
	CBA	99-99.50
	Clauspol	99.5-99.9
	Clauspol II	99.60
	SO_2 abatement	99.9
	Hydrosulfreen	99.67
	Doxosulfreen	99.98
	RAR	99.94
	LO-CAT II	99.99
	SCOT	99.5-99.99

(1) All numbers for TGCU are based on a SRU combination consisting of a 2 stage Claus as a first step.

Chapter 5 (par. 5.2.23) defines the following AELs and BAT characteristics:

- Overall sulphur recovery: 99.5-99.9% based on H_2S feed
- Utilization factor of minimum 96% including planned turnaround maintenance
- NH_3 gases: complete destruction

It should be noted that it is not clear in the current BREF how sulphur recovery efficiency is defined. Sulphur Experts define sulphur recovery efficiency as the fraction of sulphur in the feed which is recovered in the liquid sulphur stream routed to the sulphur collection pits on the unit. Consequently the sulphur recovery efficiency includes H_2S dissolved in the liquid sulphur product. However dissolved H_2S is removed form the liquid sulphur in a degassing facility and in most applications routed to the Sulphur Unit Tail Gas Incinerator where it is converted to

SO$_2$. As a result part of the material which is included in the 'sulphur recovery efficiency' is emitted as SO$_2$. Sulphur Experts estimate the contribution of the degassed H$_2$S in the sulphur recovery efficiency to be in the order of 0.01 to 0.02%. However based on a typical range of 200-500 ppmw of dissolved H$_2$S in the liquid sulphur collected from reaction the equivalent sulphur recover efficiency is rather 0.02-0.05%.

It should be noted that the SO$_2$ emission for a Sulphur Tail gas Incinerator can also be affected by the use of fuel gas containing sulphur species. Clearly this emission adds up to the emission originating from the SRU tail gas and from sulphur degassing.

Finally it should be noted that sulphur recovery efficiency only reflect operating conditions when the SRU is on stream. It does not include time periods during which sulphur is not introduced in the feed to the SRU.

7.4.   SUMMARY OF REAL PLANT OBSERVATIONS BY SULPHUR EXPERTS

7.4.1.   Overall sulphur recovery

This summary, **Table 7-2**, is based on actual sulphur recovery measurements done in more than 40 European refineries between 2004 and 2008.

The uncertainty associated to the measurement process of sulphur recovery efficiency is reported by Sulphur experts to be in the order of 0.2%. It should be noted that this uncertainty number only applies for a sulphur recovery level below 99%. Based on the uncertainty, all numbers reported by Sulphur Experts have been rounded off to the first decimal. The observed sulphur recovery ranges are also presented in **Figure 7**-**1**.

Table 7-2 Summary of SRU Datasets

Technology	Number of datasets	% Sulphur recovery (as daily average)	
		Range	*Median*
Claus 2 stage	87	92.4.0-97.8	96.1
Claus 3 stage	27	96.0-98.4	97.0
Catalytic direct Oxidation (Superclaus type)	26	95.5-99.3 (1)	98.5
Sub-dewpoint	16	98.0-99.8	99.4
Amine based	19	98.7-99.99	99.9

(1) vendor guarantee for Superclaus does not exceed 99.3%

Fig. 7-1 Observed Sulphur Recovery ranges for European plants

Sulphur Removal Efficiency
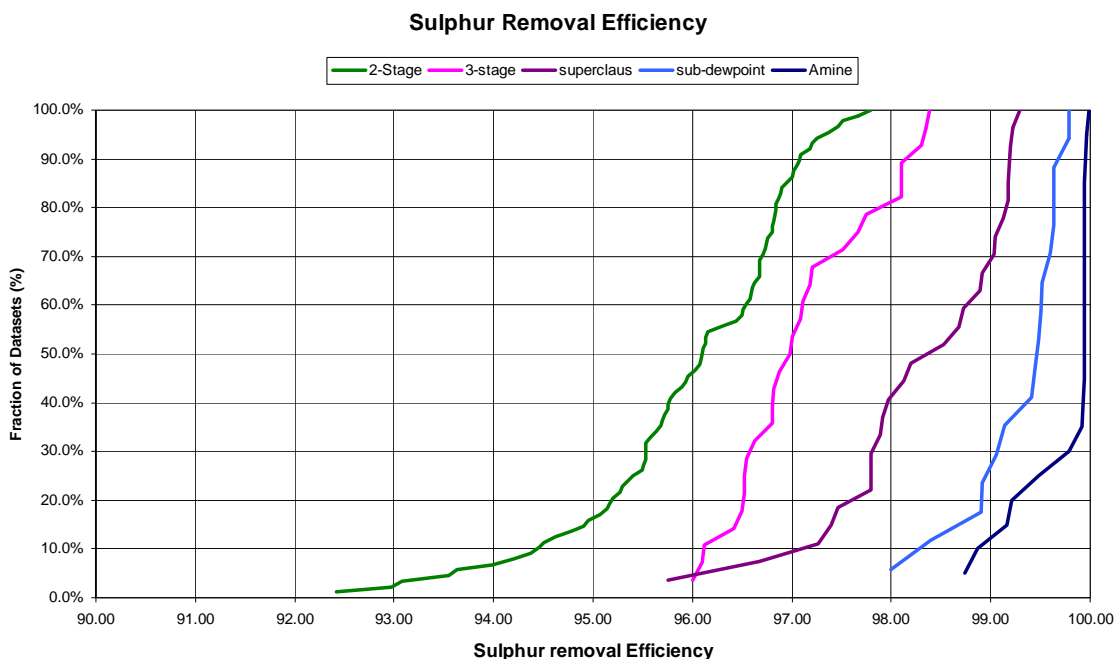
The following points provide some more background on the data:

- **Table 7-2** shows the results for European datasets. Outside Europe another 373 data-points were collected spread out over all the techniques and including natural gas treatment plants. These additional data confirmed the observed European performance ranges.
- The data-points represent the results of measurement campaigns carried out by the Sulphur Experts during a limited period of time, usually one or two days at a given time in the catalyst cycle. Therefore the data covers a wide range of catalyst life time.
- The above ranges also cover a wide range of feed composition characteristics. H_2S content in the feed ranges from as low as 50% up to almost 100%. It was found that the observed sulphur recovery showed to be rather independent from the feed H_2S content except for a feed H_2S content below 50%, which is typically not the case in refinery applications.
- Hydrocarbons and CO_2 in the feed may get converted partially to COS (from CO_2) and CS_2 (from hydrocarbons). If the Claus reactor is not equipped to hydrolyze these constituents, they will not get converted to liquid sulphur, hence this will adversely impact the sulphur recovery efficiency.
- The sulphur recovery efficiency can be affected by a number of causes. The reported range does include effects such as:
  o Catalyst deactivation over the run between two maintenance turnarounds.
  o Fouling of heat exchangers over the course of the run, resulting in increased losses of sulphur vapour in the tail gas.
- The upper part of the range coincides pretty well with theoretical performance based on ideal conditions (e.g. no variability of feed composition, start of run catalyst activity, etc.).

- Although the most of the observations and conclusions in the Sulphur Experts report are in line with the experience of industry experts there are some aspects for which there is no complete alignment. Here is a brief summary:
  - Industry believes that there are circumstances beyond the immediate control of operators (e.g. limitations imposed by unit configuration) that can limit the optimisation of a sulphur recovery plant and this is different to the view that a majority of plants can achieve maximum sulphur recovery.
  - Industry believes that there may be circumstances (e.g. of variable feed gas quality and contamination) in which it may be difficult to protect the catalyst used in catalytic oxidation units. This is not the view of Sulphur Experts.
  - According to Industry the performance of catalytic oxidation units can be depending upon the configuration with respect to the number of upstream Claus stages. According to the Sulphur Experts report there is no effect.

Conclusions

- Part of the real plant 2 and 3 stage Claus data do not meet the lower part of the current expected sulphur recovery range.
- A significant part of the observed Superclaus performance levels does not meet the ranges mentioned in Chapter 4.
- Nearly all amine based processes meet the current BREF Chapter 5 AEL range.
- Only about 50% of the sub-dewpoint units meet the Chapter 5 AEL range.
- Claus units and most catalytic direct oxidation units don't meet the Chapter 5 AEL range.
- The expected sulphur recovery level, spelled out in BREF 4.23.5.2.2. is too optimistic for some processes, mainly in the category of the oxidation and sub dew-point technology.

7.4.2. Mechanical availability

The main information on plant reliability drawn from this review can be summarized as follows:

Technology	Expected runtime, years
Claus plants	>= 3
Catalytic direct Oxidation (Superclaus type)	>=3
Sub-dewpoint	>=3
Amine based	>=3

It should be noted that in this evaluation the expected run time is mainly set by the Claus plant and it applies to well operated and managed plants.

Given the above information an annual utilization factor of minimum 94%, including planned turnarounds, is considered to be achievable. It is however proposed to replace the term 'utilization factor' by the term 'mechanical availability' as this better reflects the intention of the BREF.

7.4.3. Cost

Appendix A of the Sulphur Experts report shows a relative capital cost comparison for the various SRU technologies. Accuracy of this comparison is estimated to be +/- 30%.

The table below is a summary.

SRU technology	Relative capital cost (1)
2 stage Claus	100
3 stage Claus	109
2 stage Claus + sub-dewpoint (MCRC,CBA)	120
2 stage Claus + Superclaus	130
2 stage Claus + Sulfreen	140
2 stage Claus + amine based	194

(1) Based on a 100 t/d SRU on 80% acid gas feed (95% H_2S) and 20% Sour Water Stripper gas (56% H_2S, 43% NH_3)

7.4.4. Cross-media effects

Appendix B of the Sulphur Experts report summarizes the incremental emission of CO_2 associated to the incremental amount of SO_2 reduced by the various SRU technologies.

It can be summarized as follows:

SRU technology	Incremental t CO_2 per incremental t SO_2 reduced compared to base 2 stage Claus (1)
2 stage Claus + Superclaus	0.25
3 stage Claus 2 Stage Claus + Catalytic Oxidation	0.25 0.31
2 stage Claus + sub-dewpoint TGCU	0.55
2 stage Claus + amine based TGCU	0.75

(1) Based on a 100 t/d SRU on 80% acid gas feed (95% H_2S) and 20% Sour Water Stripper gas (56% H_2S, 43% NH_3)

It should be noted that the above data are based on the assumption by Sulphur Experts that low pressure steam which is generated on a SRU can be fully utilized as energy source. Industry practice however shows that this is often not the case as the temperature level of the steam is rather low. Consequently the marginal effect on CO_2 emissions of adding, for example an amine based unit, will be smaller than the effect shown above because of the overall higher energy losses experienced in practice.

7.5. PROPOSED AMENDMENTS TO THE BREF

- It is proposed to replace the tables in BREF 4.23.5.2.1 and 4.23.5.2.2 by the above overview of the expected overall sulphur recovery performance per category of SRU technology.

- It is proposed to define the sulphur recovery efficiency as follows: "the fraction of sulphur in the feed which is recovered in the liquid sulphur stream routed to the sulphur collection pits on the unit, therefore it includes dissolved H_2S (typically in the order of 200-500 ppmw), which is removed from the liquid sulphur product in a later stage of the process. The quoted amount of 200-500 ppmw of dissolved H_2S is equivalent to 0.02-0.05% of sulphur recovery."

- It is proposed to change the current Chapter 5 AEL range for sulphur recovery from 99.5-99.9% to 99.0-99.9% for new facilities and to 98.0-99.9% for existing units (par. 5.2.23). This proposal can be motivated as follows:

  o The lower end of the range allows most sub-dewpoint techniques to be BAT as they have a more favourable incremental cost/benefit ratio compared to more performing technologies. This provides permit authorities more flexibility in imposing other SO_2 emission reduction measures for a given refinery at optimal cost/benefit ratio.
  o The lower range for existing units is justified on the fact that revamping a unit to include a more performing technology may not be best choice from a cost/benefit ratio point of view in comparison to other potential measures for SO_2 reduction for that particular refinery.

- The 96% utilization factor is supported for the long term performance, but a value of 94% is more applicable to years in which there is a turnaround. It is proposed to replace the term 'utilization factor' by 'mechanical availability' (par. 5.2.23)

- It is proposed to include the above tables on relative cost and incremental CO_2 in BREF 4.23.2.2.

8. VAPOUR RECOVERY UNITS

8.1. INTRODUCTION AND BACKGROUND INFORMATION

EC Directive 94/63/EC prescribes the installation of vapour balancing lines and vapour recovery units (VRUs) or vapour recovery systems (VRS), during gasoline loading/unloading activities at refineries and terminals.

Vapour recovery units (VRUs) are installations designed for the emission reduction of volatile organic compounds (VOCs) which are emitted, for example, during loading and unloading operations of light products, such as gasoline, and products with equivalent volatility characteristics such as naphtha and BTX (Benzene, Toluene and Xylenes).

Techniques used in VRUs can be divided into two groups according to the method of initial separation of the VOCs from air and the subsequent recovery of the VOCs:

(1) Techniques where separation of the VOCs is achieved by pressure swing adsorption on activated carbon, absorption by lean oil washing and selective membrane separation. The separated VOCs are recovered by absorption into a product stream circulating from storage, e.g. gasoline.

(2) Techniques where VOCs are separated from the air by condensation. This can be by cooling or compression or a combination of the two processes. In these techniques separation and recovery are achieved in a single step, as the condensed VOCs can be pumped back for mixing into stored product.

Short description of those techniques:

- Absorption: the vapour molecules dissolve in a suitable absorption liquid.
- Adsorption: the vapour molecules adhere physically to activate sites on the surface of solid materials (activated carbon or zeolite) - carbon adsorption is by far the most widely installed vapour recovery technology in Europe.
- Membrane gas separation: the vapour molecules dissolve into the membrane, move by diffusion to the other side and are desorbed on the downstream side, driven by a pressure difference - these units give similar emissions to carbon adsorption, but the system is more expensive both in terms of capital investment and in operating cost.
- Refrigeration/condensation: by cooling the vapour/gas mixture the vapour molecules condense and are separated as a liquid - these were the first unit type to be installed in Europe, but were soon abandoned due to poor efficiency and high operating costs.
- Hybrid systems: combinations of VRU techniques e.g. cooling + absorption and compression + absorption + membrane separation.

CONCAWE report 90/52 [8] addressed the cost effectiveness of VRUs. It concluded that the incremental cost-effectiveness of double stage units is rather poor, ranging from 4850 to 124,300 $/incremental ton reduced (1990 cost numbers).

8.2. DISCUSSION OF BREF

8.2.1. Current BREF associated emission ranges and limits

The current BREF, in paragraph 4.21.16 (Table 4.35, including two footnotes), provides some data on the efficiency and environment performance of vapour recovery units, during the loading of motor gasoline, as shown below:

Emission values for vapour recovery plants during the loading of motor gasoline

VOC recovery technique	Emission reduction (%)	Down to (g/Nm^3)
Single stage	93-99	10
Lean oil absorption	90-95	
Activated carbon as adsorbent	95-99	
Condensation with liquid nitrogen	90	
Membrane	99	
Double stage	Near 100%	0.10-0.15

Plant type	Recovery rates (%)	Half-hourly mean values attainable in continuous operation. Total hydrocarbons	
		NMVOC[1](g/Nm^3)	Benzene (mg/Nm^3)
Single stage			
Condensation	80-95	50	1
Absorption, adsorption and membrane	90-99.5	5[2]	1
Double stage	99.98	0.15	1

[1] – The sum of hydrocarbons and methane ranges from 100 to 2500 mg/Nm^3 or higher. The methane content is only insignificantly reduced by absorptive or adsorptive processes. NMVOC stands for non-methane VOC.

[2] – If single stage plants are used as preliminary stage for gas engines, a concentration of approximately 60 g/Nm^3 is necessary for operation of the gas engine.

(The HC concentration in the uncleaned gas is approximately 1000 g/Nm^3.)

However, in the BREF paragraph 4.23.6.2, <u>achieved environmental benefits</u> are described as follows:

VRU technique	VOC removal efficiency (%)
Absorption	99-99.95
Adsorption	99.95-99.99
Membrane gas separation	99-99.9

Ranges are due to the use of 1 or 2 stages. Higher removal efficiencies are only reached with high inlet loads.

In Chapter 5, the BREF (paragraph 5.2.21) states that achieved emission levels are very dependent on the application, but a recovery range of 95-99% is considered BAT.

8.2.2. Discussion of supporting real plant data

15 VRU Datasets have been collected, as shown in **Table 8-1**.
1 is single stage lean oil absorption.
13 are single stage activated carbon adsorption.
1 is double stage: activated carbon adsorption (2 beds in series) + membrane.

Table 8-1 Summary of datasets on VRUs

Dataset No	Type of Plant	Observations
1	Single stage lean oil absorption	• Truck loading • 7 hour periods [CEM hourly averages] • VOC emissions ranging from 39.2 to 49.8 g/Nm^3
2-11	Single stage activated carbon adsorption	• Truck loading • 7 hour periods [CEM hourly averages] • VOC emissions ranging from 0.1 to 6 g/Nm^3 (<10% butane) • Only two plants have reduction efficiency data, values ranging 95.0-99.97%
12	Single stage activated carbon adsorption	• Barge loading • CEM half hourly averages • VOC emissions >10 g/Nm^3: 2% of loading time; average: 4.4 g/Nm^3
13	Single stage activated carbon adsorption	• Truck loading • 7 hour periods [Discontinuous measurement] • VOC emissions ranging from 0.1 to 6 g/Nm^3 • Benzene emission <1 mg/m^3
14	Single stage activated carbon adsorption	• Barge and railcar loading • 7 hour periods [Discontinuous measurement] • VOC emissions ranging from 0.1 to 10.8 g/Nm^3
15	Double stage: activated carbon adsorption + membrane	• Barge loading (Benzene rich naptha stream >10% m/m) • CEM half hourly averages • VOC emissions average: 4.8 g/Nm^3 • Benzene <0.7 mg/Nm^3; average: 0.1 mg/Nm^3

Reference is made to 7 data points, representing VRU applications in the UK, published in a research paper prepared for the Institute of Petroleum (now institute of Energy) [9]. These data show inlet concentrations ranging from 0.13 to 1.34 g/m^3, outlet concentrations between 0.07 and 0.74 g/m^3, the average outlet concentration being 0.53 g/m^3, and one application shows an outlet benzene emission concentration of 2 mg/Nm^3.

The data clearly confirm the statement in the BREF on methane being *'only insignificantly reduced'*, and furthermore show that ethane is not very effectively recovered either.

8.2.3. Conclusions derived from plant data

The following conclusions can be made from the above datasets.

- In general, over a period of at least seven hours the average VOC emission levels for single stage activated carbon units are within the 10 g/m^3 value stated in table 4.35 of the BREF, and meet NMVOC of 5 g/m^3. We do not have data for single stage membrane units but would expect comparable performance.

Only two plants have reduction efficiency data. These show efficiencies in line with table 4.35 of the BREF, but lower than the range quoted in paragraph 4.23.6.2.

- Benzene emission data available range from 0.1 to 2 mg/Nm^3.

- The averaged VOC emissions for the single stage lean oil absorption unit are above the 10 g/m^3 value stated in Table 4.35 of the BREF.

- The VOC emissions for the double stage unit meet 1 mg benzene/m^3 on average during entire loading, but do not meet NMVOC 0.10-0.15 g/m^3 level mentioned in table 4.35 of the BREF. This is related to the specific operation at more than 10% benzene in the loaded naphtha product. For gasoline loading, a NMVOC level of 0.15 g/m^3 is deemed achievable, taking into account the observations from the IP paper which shows insignificant methane reduction.

8.3. PROPOSED AMENDMENTS TO BREF

Based on the conclusions described above, the following amendments are proposed:

a. Paragraphs 4.21.26 and 4.23.6.2

- It is proposed not to use percentage reduction performance levels as AEL, but rather as an indicator of performance. To monitor the percentage reduction or recovery it is necessary to measure the inlet concentration, which is far less practical than monitoring the outlet concentration. Therefore it is proposed to use the outlet concentration as a parameter for the AEL, including in chapter 5. This is also in line with the Gothenburg Protocol [10].

- It is proposed to base the AEL on an average performance over the entire daily period of VRU operation. This is in line with the requirements of the Gothenburg Protocol, Annex VI, paragraph 34 (d), stating '*In the case of continuous measurements, as a minimum requirement, compliance with the emission standards is achieved if daily mean does not exceed the limit value during normal operation and no hourly average exceeds the limit values by 150%'.*

- The proposed AELs can be summarized as follows:

  o Single stage: VOC average outlet concentration of 10 g/m^3; benzene average outlet concentration of 5 mg/m^3
  o Double stage on gasoline loading: NMVOC average outlet concentration of 0.15 g/m^3
  o Double stage carbon adsorption on streams other than gasoline: VOC average outlet concentration of 5 g/m^3

- It is proposed to delete the first footnote at the bottom of table 4.35 from the BREF ('*The sum of hydrocarbons and methane ranges from 100 to 2500 mg/Nm³')* as it is not consistent with emission levels for NMVOC in the table.

- Lean Oil absorption does not seem to meet an AEL level of 10 g/m³. It is proposed to mention this in table 4.35 as a footnote.

- It is proposed to delete the table in paragraph 4.23.6.2 as it is not consistent with table 4.35 in paragraph 4.21.16.

- It is proposed to add the following item on cost: "the incremental cost-effectiveness of double-staged VRUs is rather poor, ranging from 4850 to 124,300 $/incremental ton reduced, according to a 1990 CONCAWE study [8]".

b. Paragraph 5.2.21

- It is proposed to replace the AEL range on percentage recovery by the AEL levels mentioned in the above proposed amendments to Chapter 4.

- It is further proposed to include the comment and information on double-stage VRUs, presented above as amendment to Chapter 4.

9. SUMMARY OF AMENDMENTS

Proposed amendments for performance ranges or AELs are based on daily averages unless specified otherwise. Performance ranges for emission concentration are defined in terms of mg/Nm^3 dry gas @ 3% excess O_2, unless specified otherwise. In all cases the AEL values should comprise a range and where possible the range should be subdivided to make clear that differences in technology and in operating conditions can influence the AEL and hence the consideration of a BAT for each installation.

9.1. GENERAL

1. Make clear that AELs are only applicable to normal operations, excluding start-up, shutdown and also excluding special operations of short duration, such as soot-blowing, steam-air decoking, chemical radiant cell tube cleaning or sand scouring of heat transfer surfaces.
2. Provide Chapter 5 AELs per BAT technique and not for any combination of techniques.

9.2. COMBUSTION NO$_X$

9.2.1. Low NO$_X$ burners for heaters and boilers

NOTE: The effect of operating conditions, air pre-heat temperature, bridge temperature and fuel composition can greatly influence where a burner emission falls in the AEL range. A full methodology for accounting for these effects is described in Appendix I.

9.2.1.1. Chapter 4 performance ranges

1. Replace current paragraph 4.10.4.1. performance range for gas fired Low NO$_x$ burners from 30-150 mg/Nm^3 to 50-200 mg/Nm^3 for existing installations and to 50-150 mg/Nm^3 to new installations. The upper end of the range (200) is for existing installations using a high air preheat (up to 200°C).
2. Replace current paragraph 4.10.4.1. performance range for dual firing low NO$_x$ burners on heavy liquid from 150-400 mg/Nm^3 to 300-450 mg/Nm^3, applicable to a liquid firing rate of 50-100% on total heat fired. Include a comment that this AEL range is only achievable for liquid fuels with a fuel-bound nitrogen content below 0.5%.
3. Limit applicability of current paragraph 4.10.4.1 performance range of 100-250 mg/Nm^3 for dual fired Low NO$_x$ burners on liquid fuel to light liquid fuels with a fuel-bound nitrogen content =< 0.01 wt %.

9.2.1.2. Chapter 5 AELs

1. Add a discussion of the effect of operating and fuel parameters on NO$_x$ emissions as exemplified in the BEES approach [11].
2. Delete the current paragraph 5.2.10 AEL range of 20-150 mg/Nm^3 for gas fired heater and boilers.
3. Add a new AEL range to paragraph 5.2.10: 50-200 mg/Nm^3 for existing gas fired low NO$_x$ burners and to 50-150 mg/Nm^3 to new gas fired Low NO$_x$ burners.

4. Delete the current paragraph 5.2.10 AEL range of 55-300 mg/Nm^3 for liquid fuel fired heaters and boilers.
5. Add a AEL range for Low NO$_x$ burners on dual firing to paragraph 5.2.10: 300-450 mg/Nm^3, applicable to a liquid firing rate of 50-100% on total heat fired. The latter proposal is also known as the majority fuel concept. Include a comment that this AEL range is only achievable for liquid fuels with a fuel-bound nitrogen content below 0.5%.
6. Delete the current paragraph 5.2.10 AEL range of 5-20 mg/Nm^3 for PM (particulate matter) from combustion.
7. Add a new AEL range for PM emission from dual fired Low NO$_x$ burners to paragraph 5.2.10: 5-50 mg/Nm^3 as a monthly average, applicable to a liquid firing rate of 50-100% on total heat fired. The latter proposal is also known as the majority fuel concept. Include a comment that this AEL range is only achievable for liquid fuels with an asphaltene content below 10% and ash content below 0.05%.

9.2.1.3. Applicability

Include in paragraphs 4.10.4.1 and 5.2.10 that the lower end of the AEL range on gas fired Ultra Low NO$_x$ burners is only achievable under narrow circumstances:

a) May preclude the application of combustion air preheat.
b) Fired by natural gas or light gas (without C3+) without any ammonia or fuel-bound nitrogen. Replacing refinery fuel gas by natural gas firing is not considered an effective measure as it would result in an excess of refinery fuel gas for which there would be no other outlet than destruction in the flare.
c) Fuel gas cleaning systems are provided, such as coalescing filters and/or heat tracing of the fuel gas supply piping and in some cases stainless steel piping downstream of the filters.
d) With precise control of the oxygen concentration at the firebox outlet for forced draft applications. This may not be feasible for natural draft applications.
e) No flame instability is encountered for the specific application.

9.2.1.4. Cross-media effects

Include in paragraphs 4.10.4.1 and 5.2.10 that a reduction of air preheat by 200°C is equivalent to a 10% decrease in energy efficiency.

9.2.2. SNCR and SCR for heaters and boilers

9.2.2.1. Chapter 4 performance ranges

1. Delete the performance levels for the NO$_x$ outlet concentration of SNCR applications on heaters and boilers (paragraphs 4.10.4.6 and 4.23.3.2).
2. Replace the performance range for the NO$_x$ emission reduction efficiency for SNCR from 40-70% to 25-70% (paragraphs 4.10.4.6 and 4.23.3.2). This reduction efficiency range is only applicable to inlet NO$_x$ concentrations above about 200 mg/Nm^3.
3. Replace the performance range of 90-94% for SCR applications (par. 4.10.4.7) by a range of 80-95%. This reduction efficiency range is only applicable to inlet NO$_x$ concentrations above about 200 mg/Nm^3.

9.2.2.2. Chapter 5 AELs

1. Add a new AEL range to paragraph 5.2.10: a NO_x reduction efficiency of 25-70% for SNCR applications. This AEL range is only applicable to inlet NO_x concentrations above about 200 mg/Nm^3.

2. Add a new AEL range to paragraph 5.2.10: a NO_x reduction efficiency of 80-95% for SCR applications. This AEL range is only applicable to inlet NO_x concentrations above about 200 mg/Nm^3.

9.2.2.3. Applicability

1. The requirements for a high NO_x reduction efficiency include:

- Good mixing between the urea and the stream of combustion products,

- Adequate temperature window in the mixing region,

- Adequate residence time (at least 0.2 to 0.5 s in the region of injection),

- No impingement of the injected chemical against the furnace tubes.

Thus, application of the SNCR technique in existing furnaces and boilers requires well chosen injection locations and a mixing region with appropriate temperature and size to allow for sufficient NO reduction. In practice, this is very difficult to achieve as temperature profile in the boiler varies with boiler load.

2. Change the required temperature range for SNCR (par 4.10.4.6) to 870-1090°C.

3. Typically NO_x removal performance increases at higher ammonia slip levels. However for heaters burning sulphur containing fuels, the ammonia slip could lead to formation of ammonium sulfates that tend to deposit further downstream on cold parts (tubes of furnace, convective section, boiler economizer). These deposits could lead to accelerated corrosion. This risk of ammonium sulfate deposition imposes to operate with a low ammonia slip, hence decreasing the efficiency of the NO_x reduction.

4. Expected NO_x reduction performance of SCR on existing heaters and boilers depends on the amount of catalyst and how the unit can be fitted into existing flue gas duct systems.

9.2.2.4. Cross-media effects

Replace all existing ranges for ammonia slip on SCR by a range of 2-20 mg/Nm^3 (par. 4.10.4.7, 4.23.3.3 and 5.2.10).

9.3. FLUIDISED CATALYTIC CRACKING UNITS

9.3.1. NO$_x$ emissions from units with a CO Boiler (COB) and full burn units without a COB

9.3.1.1. Chapter 4 performance ranges

1. All emission performance ranges to be based on daily average at the least (for reference in the US the averaging periods are 7-day for rolling short term and 365 days for long term average). The current, tight half-hourly average described in Chapter 4.5.1 is inconsistent with the averaging time stated in Chapter 5 for the same BAT AEL range. Furthermore it is extremely difficult to meet half-hourly plant limits in case of variations of operating conditions or abnormal processing events (paragraphs 4.5.1, 4.5.3 and 5.5).

2. Make an exception to the current performance range of 300-700 mg/Nm^3 for full burn applications with antimony additions. Amend upper range to 1000 mg/Nm^3 in case of injection of antimony (residual feedstock cracking), which is very likely to significantly increase NO$_x$. While it is noted that such levels of NO$_x$ emissions are considered very high it is proposed to document this as an upper range for unabated NO$_x$ emissions from a FCCU (paragraph 4.5.1).

3. Amend the current upper performance range for partial burn data from the current 100-500 mg NO$_x$/Nm^3 (chapter 4.5.3) to 100-800 mg/Nm^3 to account for higher emissions resulting from COB use for steam production (high supplementary fuel consumption) (paragraph 4.5.3).

9.3.1.2. Chapter 5 AELs

1. Align AEL for full burn units with the AEL proposed for paragraph 4.5.1 (300-700 mg/Nm^3) and include a separate AEL for residual feedstock cases with antimony injection (300-1000 mg/Nm^3) (paragraph 5.2.5).

2. Align AEL for partial burn units to the AEL proposed for paragraph 4.5.3 (100-800 mg/Nm^3) and document the distinction between a COB being used as an incinerator versus a steam boiler, as described in section 5.1.1 of this report (BREF paragraph 5.2.5).

3. Add the following comments (paragraph 5.2.5) about processing residual feedstock: "The processing of residual feedstock can have specific environmental impacts, including an increase in NO$_x$ emissions, as described in section 5.1.2 of this report. Hence in the case of a unit running predominantly residual feedstock through the FCC the current BREF AELs may not be met for the following reasons:

   o Potential consequences of the high metals content include: increased NO$_x$ emissions due to antimony additions.
   o Consequences of increased feed nitrogen content include: increased production of NO or of NO$_x$ precursors such as NH$_3$ and HCN".

9.3.1.3. Applicability

1. Add the following comment about the consistency of FCC performance: "The NO_x emission from a FCC unit can increase over time as the quality of air and catalyst mixing in the regenerator deteriorates as as a result of wear. For example, internal mechanical damage could occur towards the end run of the unit and this could significantly increase all unit emissions (NO_x, SO_x and PM)" (paragraphs 4.5.1 & 4.5.3).

9.3.1.4. Cross-media effects

1. Add the following comment under Cross-media effects: "In full burn mode, when excess O_2 is reduced to around 0.5%, NO_x production is dramatically reduced; however, SO_x content is typically increased. A possible explanation of the increased SO_x is that with less O_2 the coke is not completely burned off the catalyst. The catalyst then generates more coke, and increased coke production correlates to larger SO_x production."

9.3.2. CO emissions of FCC with a COB and full burn units without a COB

9.3.2.1. Chapter 4 performance ranges

1. Add comment that the performance range of 35-250 mg/Nm^3 is strictly only met if the regenerator excess O_2 is above 2%. In cases where the unit is running at O_2 <2% these performance ranges may not be met due to significantly higher CO emissions at low O_2 levels (paragraph 4.5.1).

2. Amend the averaging time for the performance range on CO from full burn units to a daily average (paragraph 4.5.1) in order to stay consistent with other BREF AELs and with Chapter 5 of the BREF.

9.3.2.2. Chapter 5 AELs

1. Amend the AEL range in paragraph 5.2.5 for full burn operation to 35-250 mg/Nm^3 (consistent with the range proposed in paragraph 4.5.1) and to 50-400 mg/Nm^3 for units with a COB (consistent with the existing range in paragraph 4.5.3).

2. Include the comment: "The proposed AEL range for full burn operation on the regenerator excess O_2 control may not be met if the regenerator is operated at O_2 levels below 2%, however this operating condition generally lowers NO_x emissions" (paragraph 5.2.5).

9.3.3. SO$_x$ Reducing Additives (SRA)

9.3.3.1. Applicability

1. Add the following comment regarding factors affecting SO_x reduction efficiency: "The outlet SO_x emission concentration achieved with the use of SRAs is highly dependent on SO_x inlet concentrations, amount of SRA that can be used and the unit operating mode" (paragraph 4.5.10.1).

2. Add the following comment under the applicability section: "The typical upper limit of SRA addition rate is about 10% of the fresh catalyst addition. Industry

experience shows that above this addition rate, negative unit yield impacts are likely" (paragraph 4.5.10.1).

3. Amend the following sentence in the BREF text as it is not accurate: "SO_x Reducing Additive is more efficient in full burn mode. However, full burn implies more SO_x and NO_x formation than partial combustion mode". SO_x emission is similar for full and partial burn operation, whereas NO_x leaving the regenerator in partial burn mode is usually lower compared to full burn, but combustion of the NO_x precursors in the COB can result in higher stack NO_x emissions for partial burn (paragraph 4.5.10.1).

4. Add the following paragraph regarding averaging period for emissions: "When defining AELs for SO_x emissions and performance of SRAs, the averaging period is an important factor since there can be a wide variation of parameters which affect the SO_x, such as feedstock sulphur content and type of feed sulphur. The proposal is for a monthly average or at the least a 7 day rolling average to account for the variation in the feed sulphur properties" (paragraph 4.5.10.1).

9.3.3.2. Cross-media effects

1. Add the following remarks to paragraphs 4.5.10.1 and 5.2.5 regarding the cross media effects and operational issues associated with SRAs:

- The potential increase of attrition results in more fine particles and hence potential increased PM emissions.
- Conditions favourable to increase SRA efficiency may lead to increased uncontrolled NO_x emissions.

9.3.4. NO_x Reducing Additives (NRA)

9.3.4.1. Chapter 4 AELs

1. Add NO_x Reducing Additives (NRAs) as a technique that has moved beyond "emerging", but is not yet fully proven. For all full burn applications. Setting BREF AELs is not possible at this early stage since observed performance has a wide range from ineffective up to 60% reduction in NO_x concentration.

2. Add the following comment: "For partial burn units there are currently no effective NRAs available; this is due to the fact that in partial burn different species of nitrogen are involved in NO_x formation, i.e. NO_x precursors HCN and NH_3 which are converted to NO_x in the COB."

9.3.5. Low NO_x Combustion Promoter (COP) additives

9.3.5.1. Chapter 4 performance ranges

1. Add a section on Low NO_x (non-Pt) COP as a technique, which has the potential to control CO and afterburning but at a lower NO_x level compared to the use of Pt-based COPs. It is only applicable in full burn units.

2. Add the following paragraph on optimising the use of Combustion Promoters: "If NO_x concentrations need to be reduced then the first control option is to

reduce the platinum load in the catalyst bed, either through minimising the addition rate or reducing the platinum content of the additive. However as afterburning needs to be kept under control, this option can be limited".

9.3.5.2. Chapter 5 AELs

1. As above, include Low NO_x COP as a technique, which has the potential to control CO and afterburning but at a lower NO_x level compared to the use of Pt-based COPs. It is only applicable in full burn units.

9.3.5.3. Applicability

Include the following Applicability notes on Low NO_x COP:

1. Low NO_x COP is an option for NO_x reduction in systems already using a platinum based COP to control afterburning.
2. Low NO_x COP is not applicable at all for partial burn FCCs.
3. To achieve an acceptable level of afterburning by using low NO_x COP it may be necessary to significantly increase the dosage rate compared to conventional Pt based COP and at high dosage rates there may be a NO_x penalty.

9.3.6. Selective Non-Catalytic Reduction (SNCR)

9.3.6.1. Chapter 4 performance ranges

1. Amend the current Emission Reduction Efficiency for SNCR from 40-60% to 20-65% to better reflect the actual performance range of the technology as shown in the datasets provided. (paragraph 4.5.8.2)

2. Amend the ammonia slip range to 2-20 mg/Nm^3 as per current paragraph 4.23.3.3 of the BREF, to ensure consistency throughout the document. There is a relationship between the achievable NO_x removal efficiency and ammonia slip: a higher NO_x removal performance requires more ammonia, resulting in a higher ammonia slip. (paragraph 4.5.8.2)

9.3.6.2. Chapter 5 AELs

It is proposed to include the above proposals for paragraph 4.5.8.2 in paragraph 5.2.5.

9.3.6.3. Applicability

- The reduction efficiency is dependent on: CO Boiler residence time at the required temperature range for SNCR, CO Boiler temperature profile, inlet temperature, and allowable NH_3 Slip. The latter is the only parameter which can be controlled by the operator. The other factors are fixed characteristics of the installation. (paragraph 4.5.8.2)

  Add the following comment to paragraph 4.5.8.2: "During specific non-routine operational episodes, e.g. when the FCCU is in operation but the COB is shutdown, emissions could differ significantly from the performance during normal operation. Such special operational episodes are not covered by the AEL range."

- SNCR applications are most effective in the flue gas temperature window of 870-1090°C. The effective temperature window can be extended down to about 700°C by addition of hydrogen but this application is limited to the use of ammonia as the SNCR reagent. The process of vaporization and dissociation of urea precludes the use of hydrogen with urea-based SNCR. (paragraph 4.5.8.2)

- SNCR cannot be applied for combustor type COBs which are operated at a minimum flue gas temperature of 1090°C and therefore SNCR is not BAT for this type of equipment. (paragraph 4.5.8.2)

- The BREF also states in paragraph 4.5.8.2 that this technology "is applicable in partial combustion FCCs with CO boiler and retrofitting in existing CO boilers is relatively simple". It is proposed to replace this sentence by the following comments: "As the reduction efficiency is very dependent on the COB configuration and residence time, application of SNCR in retrofits of FCCs with a CO Boiler may not result in optimal performance. It can also be applicable to full combustion units either applied in the regenerator overhead line using hydrogen addition or in an auxiliary fired boiler. Space requirements are mainly related to NH_3 storage".

9.3.6.4. Cross-media effects

- One issue that is of particular concern with SNCR applications in FCCUs is the potential for an associated increase in CO emissions. At the lower end of the SNCR operating temperature range ammonia can inhibit CO oxidation. Therefore, if the COB temperature is low, CO emission concentrations could increase and this should be a consideration when considering the suitability of SNCR in retrofit applications.

- Another issue is the potential increase in N_2O, a greenhouse gas (GHG) which can be formed in the SNCR process, especially if urea is used. The magnitude of the increase seems to be related to the NH_3/NO_x molar ratio and the operating temperature. The applications using H_2 may result in higher N_2O concentrations.

9.3.7. Selective Catalytic Reduction (SCR)

9.3.7.1. Chapter 4 performance ranges

It is proposed to change the range for ammonia slip in paragraph 4.5.8.1 from <2-10 mg/Nm^3 to 2-20 mg/Nm^3, consistent with our proposed amendment for the application of SCR on fired heaters and boilers and with the BREF section 4.23.3.3 on waste gas treatment.

9.3.7.2. Chapter 5 AELs

It is proposed to change the range for ammonia slip from 2-5 mg/Nm^3 to 2-20 mg/Nm^3, consistent with the proposed amendment for the application of SCR on fired heaters and boilers.

9.3.7.3. Applicability

1. It is proposed to amend the comment in the BREF paragraph 4.5.8.1 which states "run time of SCR unit can be up to 6 years". The shutdown frequency for cleaning is highly dependent on the unit configuration and can be as low as every 7 months. Fouling by salts or catalyst fines causes a build up of pressure drop over the catalyst bed. The pressure drop at which the SCR must shut down is very FCCU specific. Furthermore, the rate of catalyst fouling can be affected by the location of the SCR in the process scheme (i.e. it may be less prone to plugging if installed downstream of ESP or other particulate control device). The above mentioned AEL is only applicable to normal operations, excluding shutdown periods for cleaning.

2. Include the following comment in paragraph 4.5.8.1: "The application of a SCR could reduce the potential for energy recovery by expander turbines, which is BAT for energy recovery. The operation of a SCR unit increases the pressure drop over the regenerator overhead circuit and is also prone to a build-up of pressure drop over time, thereby limiting the available operating window for a turbine expander, particularly in existing facilities with fixed pressure profiles".

3. It is proposed to amend the comment in paragraph 4.5.8.1 of the BREF which states that "retro-fit application is highly applicable". It is proposed to include the following comment: "SCR requires a temperature range of typically 300-400°C. This can complicate retrofit applications where the auxiliary fired boiler/ COB circuits or the waste heat boiler system regenerator flue gas system may have to be modified to establish the required inlet temperature for SCR."

9.3.8. Scrubbers

9.3.8.1. Chapter 4 performance ranges

1. It is proposed to replace the parameter 'SO_x' (BREF paragraph 4.5.10.2, table 4.10) by 'SO_2'.

2. It is proposed to remove the reduction efficiencies for PM, SO_2 and NO_x from table 4.10 in the BREF paragraph 4.5.10.2 as it is not the most suitable performance parameter of a WGS.

3. It is proposed to amend the current performance range for SO_2 (BREF paragraph 4.5.10.2, table 4.10) of 10-400 mg/Nm^3 outlet SO_2 emissions to 60-400 mg/Nm^3.

4. It is proposed to amend the current performance range for PM (BREF paragraph 4.5.10.2, table 4.10) of <10-35 mg/Nm^3 to 30-60 mg/Nm^3 PM outlet emissions.

5. It is proposed to remove the 93% removal efficiency for SO_2 and PM as currently stated in the BREF paragraph 4.5.10.3 and to refer to table 4.10 of the BREF section 4.5.10.2.

9.3.8.2. Applicability

1. In the BREF paragraph 4.5.10.2 it is stated that "a suitably designed wet scrubbing process will normally provide an effective removal efficiency of both SO_2/SO_3 and particulates". It is proposed to add the following comment "However, wet scrubbers have a low removal efficiency of SO_3. Typical SO_3 removal values are 25 to 50%; this is much lower than removal efficiency of SO_2 and particulates. In addition, particulate removal efficiency depends on the type of wet scrubber".

2. It is proposed to amend the cross-media effect stated in the BREF paragraph 4.5.10.2 as "wet scrubbing processes generate low pressure drop, operate at low temperature and do not create solid deposition problems". It is proposed to include the following comment: "The performance of Wet Gas Scrubbers can be affected by deposition problems occurring in the course of a five year run. The amount of deposition depends on the inlet catalyst and SO_2 load to the scrubber, the quality of the make-up water, the operating pH of the scrubber and level of purge applied to the scrubbing slurry. The deposits essentially comprise catalyst dust that settles at low points and on mist eliminators and hardness deposits such salts of calcium etc that precipitate as the operating pH is increased to achieve high SO_2 removal efficiency."

3. It is proposed to remove the following statement from the BREF paragraphs 4.5.10.2 and 4.5.10.3: "These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide etc.".

4. It is proposed to remove the following statement from the BREF paragraph 4.5.10.3: "Venturi scrubbers are widely applied for the treatment of small flows".

9.3.9. Third stage backflow filters

9.3.9.1. Chapter 4 performance ranges

1. It is proposed to add third-stage backflow filters as an emerging BAT in the BREF document.

9.3.9.2. Chapter 5 AELs

As above.

9.3.9.3. Applicability

1. The third stage backflow filters have very limited applicability for FCCs as they have only been proven on a small flue gas system with a flow of 2100 tons/day, and not on the large scale of a typical FCC unit.

2. The filter can remain in operation during FCCU upset conditions, start-up and shut-down conditions, which allows for control of emissions during these events.

3. There is a process safety concern with full flow filters. A potential blockage could lead to over-pressure in the regenerator system and it may be necessary to provide specific safety devices (e.g. bypasses).

9.3.10. Electrostatic Precipitators (ESPs)

9.3.10.1. Chapter 4 performance ranges

1. Amend the averaging time for the performance range to be based on a monthly average to account for start-up and operational peaks (occurring at <5% of the time).

2. Exclude the emission reduction efficiency of >99.8% from the BREF as this is not a suitable measure of the performance of the ESP.

9.3.10.2. Chapter 5 AELs

1. Include the same amendments as above for paragraph 4.5.9.2.

9.3.10.3. Applicability

1. Include the following comment: "For safety reasons the ESP cannot be kept in service during start-up and shut-down operations of the FCC unit. This is described in more detail below under cross media effects. It is proposed that the BREF AELs should not be applicable for these periods."

9.3.10.4. Cross-media effects

1. Add the following paragraphs regarding safety concerns when operating the ESP.

   There is incremental risk of an explosion in the event of a combustible mixture passing through the electrically charged ESP. This could occur during FCC unit restart or unplanned unit conditions. Industry experience shows that in the past two types of fires or explosions have been observed in ESPs, causing extensive damage. The first type is a fire in the dust collected on the ESP collecting plates or hoppers (carbon being the combustible material). The second type of fire occurs when a flammable mixture of gases (typically CO or natural gas) explodes [7].

   Adequate operating procedures are required to mitigate this real risk. A very effective risk mitigation measure consists in a start-up or shut down sequence of the FCC unit without energizing the ESP, leaving it electrically isolated. In such procedure the ESP is not energized until the flue gas it receives is fully combusted, by either the regenerator or the CO boiler. Consequently higher emissions of particulates will occur during start-up operations.

2. Add the following comment under applicability: "To achieve the BREF lower AEL of 10 mg/Nm^3 a residence time of 30 seconds or more is needed, requiring an ESP of a significantly larger size than current units."

3. Remove the following text in the BREF which states that "ESP efficiency is not dependent on particle size" (paragraph 4.5.9.2).

4. Add the following comment under applicability: "ESP performance will degrade from start to the end of the run. Since minimal maintenance can be done to the ESP without an outage, degradation in performance is expected" (paragraph 4.5.9.2).

5. Remove the following comment "particulate emissions from the FCC can be reduced to 1.1-2.3 kg/h" (paragraph 4.5.9.2).

9.3.11. Third stage cyclones

9.3.11.1. Chapter 4

Replace paragraph 4.5.9.1 on additional cyclones by the following:

Description of technique

Conventional technology for flue gas particulate removal includes electrostatic precipitators and wet scrubbers. New cyclonic technology, like Third-Stage Separators (TSS), provides an alternative as a viable solution for FCC emissions control, while also reducing the plugging tendency of some techniques used to reduce NO_x emissions such as selective catalytic reduction (SCR) technology.

A multistage cyclone is a common choice for removal of particulates: these are conventional cyclones, fitted externally to the regenerator but operating on the same principle as the first and second stage cyclones installed in the regenerator. The multistage cyclones are operated at high velocity and recovered catalyst is returned to a dust hopper.

The performance varies considerably, mainly depending on the Particle Size Distribution (PSD), the amount of catalyst fines emitted by the regenerator and the performance of the regenerator cyclones. Under normal unit operating conditions, the overall multistage cyclone efficiency is affected by the following factors:

- Particle size distribution
- Concentration of solids in the gas and the particle-density
- Cyclone geometry details
- Vapour flow rate, -density and viscosity
- Mechanical condition of the cyclones (roundness, wall-roughness, leaks etc.)

9.3.11.2. Achieved environmental benefits

Inlet TSS	100-400 mg/Nm^3
Outlet TSS	50-400 mg/Nm^3, can be <50 depending on the inlet particle distribution and load.
Reduction efficiencies for loading <400 mg/Nm^3	>75% provided particle size distribution with median (by mass) >5 μm

By reducing the particulate content in the air, metal emissions are also reduced. Multistage cyclones with swirl tubes are generally efficient at removing about 50% of particles sized greater than 3 microns. A higher removal efficiency is achievable for particles with a larger size, approaching 100% removal for particles of 10 microns and larger.

9.3.11.3. Cross-media effects

Catalyst fines recovered are considered as waste.

9.3.11.4. Operational data

It generates a pressure drop in the flue gas.

9.3.11.5. Applicability

Applicable to any FCC.

9.3.11.6. Economics

Economics of disposal of the fine catalyst is around EUR 120-300 per tonne, including transportation.

9.3.12. Amine treating

1. Replace the current performance ranges in BREF paragraphs 2.10, 4.23.5.1 and the current AEL range in paragraphs 5.2.10 and 5.2.23 by the table below:

Amine Scrubber pressure, bara	Proposed ranges for H_2S in fuel gas, mg/Nm^3
50	2-15
20	4-40
3.5	20-220

2. Increase the upper BAT AEL range for SO_2 from gas firing applications from 20 mg/Nm^3 to 35 mg/Nm^3, dry @ 3% O_2 (par. 5.2.10).

3. Include a note that the proposed upper range of 35 mg/Nm^3 for SO_2 cannot be met for applications at a scrubber operating pressure lower than 3.5 bara and a fuel gas H_2 content above 45%.

4. Include a note that fuel gas may contain sulphur in other forms than H_2S, for example, as mercaptans (originating from thermal cracking processes) and COS (mainly originating from FCC units) Mercaptans are not removed by amine treating and non-refining applications such as natural gas treating may require after-treatment steps. COS is difficult to remove.

9.3.13. Sulphur Recovery Units (SRU)

9.3.13.1. Chapter 4 performance ranges

1. It is proposed to define the sulphur recovery efficiency as follows: "the fraction of sulphur in the feed which is recovered in the liquid sulphur stream routed to the sulphur collection pits on the unit, therefore it includes dissolved H_2S (typically in the order of 200-500 ppmw), which is removed from the liquid sulphur product in another stage of the process. The quoted amount of 200-500 ppmw of dissolved H_2S is equivalent to 0.02-0.05% of sulphur recovery."

2. Replace the tables containing performance ranges for the overall sulphur recovery in par. 4.23.5.2.1 and 4.23.5.2.2 by the following overview of the expected overall sulphur recovery performance per category of SRU technology.

Technology	*Range for overall sulphur recovery %*
Claus 2 stage	92.4-97.8
Claus 3 stage	96.0-98.4
Catalytic direct Oxidation (Superclaus type)	95.5-99.3
Sub-dewpoint	98.0-99.8
Amine based	98.7-99.99

9.3.13.2. Chapter 5 AELs

1. It is proposed to define the sulphur recovery efficiency as follows: "the fraction of sulphur in the feed which is recovered in the liquid sulphur stream routed to the sulphur collection pits on the unit, therefore it includes dissolved H_2S (typically in the order of 200-500 ppmw), which is removed from the liquid sulphur product in another stage of the process. The quoted amount of 200-500 ppmw of dissolved H_2S is equivalent to 0.02-0.05% of sulphur recovery."

2. Replace the current Chapter 5 AEL range for sulphur recovery from 99.5-99.9% to 99.0-99.9% for new facilities and to 98.0-99.9% for existing units (par. 5.2.23).

9.3.13.3. Applicability

Replace the term 'utilization factor' by the term 'mechanical availability'.

9.3.13.4. Cross-media effects

1. The incremental CO_2 emission for the various SRU techniques can be summarized as follows:

SRU technology	Incremental t CO_2 per incremental t SO_2 reduced compared to base 2 stage Claus (1)
2 stage Claus + Superclaus	0.25
3 stage Claus 2 Stage Claus + catalytic oxidation	0.25 0.31
2 stage Claus + sub-dewpoint TGCU	0.55
2 stage Claus + amine based TGCU	0.75

(1) Based on a 100 t/d SRU on 80% acid gas feed (95% H_2S) and 20% Sour Water Stripper gas (56% H_2S, 43% NH_3)

It should be noted that the above data are based on the assumption that the low pressure steam which is typically generated on a SRU can be fully utilized as energy source. However this is not always the case as the temperature level of the steam is rather low. Consequently the marginal effect of CO_2 of some processes can be overstated.

9.3.13.5.   Cost information

1. Include the following table showing a relative capital cost comparison for the various SRU technologies. Accuracy of this comparison is estimated at +/- 30%.

SRU technology	Relative capital cost (1)
2 stage Claus	100
3 stage Claus	109
2 stage Claus + sub-dewpoint (MCRC,CBA)	120
2 stage Claus + Superclaus	130
2 stage Claus + Sulfreen	140
2 stage Claus + amine based	194

(1) Based on a 100 t/d SRU on 80% acid gas feed (95% H_2S) and 20% Sour Water Stripper gas (56% H_2S, 43% NH_3)

9.3.14.   Vapour Recovery Units (VRU)

9.3.14.1.   Chapter 4 performance ranges

1. It is proposed not to use percentage reduction not as a performance level but rather as an indicator of performance. To monitor the percentage reduction or recovery it is necessary to measure the inlet concentration, which is far less practical than monitoring the outlet concentration. Therefore it is proposed to use the outlet concentration as a parameter for the performance (par. 4.21.16 and 4.23.6.2).

2. It is proposed to base the performance level on an average performance over the entire daily period of VRU operation. This is in line with the requirements of the Gothenburg Protocol, Annex VI, paragraph 34 (d) [10].

3. The proposed performance ranges can be summarized as follows:
    - Single stage: VOC average outlet concentration of 10 g/m^3; benzene average outlet concentration of 5 mg/m^3
    - Double stage on gasoline loading: NMVOC average outlet concentration of 0.15 g/m^3
    - Double stage carbon adsorption on streams other than gasoline: VOC average outlet concentration of 5 g/m^3

4. It is proposed to delete the first footnote at the bottom of table 4.35 from the BREF ('*The sum of hydrocarbons and methane ranges from 100 to 2500 mg/Nm^3')* as it is not consistent with emission levels for NMVOC in the table.

5. Lean Oil absorption does not seem to meet a performance level of 10 g/m^3. It is proposed to mention this in table 4.35 as a footnote.

6. It is proposed to delete the table in paragraph 4.23.6.2 as it is not consistent with table 4.35 in paragraph 4.21.16.

9.3.14.2. Chapter 5 AELs

1. It is proposed to replace the AEL range on percentage recovery by the AEL levels mentioned in the above proposed amendments to Chapter 4 (par. 5.2.21).

2. It is further proposed to include the comment and information on double-stage VRUs, presented above as amendment to Chapter 4.

9.3.14.3. Cost information

1. It is proposed to add the following item on cost: 'the incremental cost-effectiveness of double-staged VRUs is rather poor, ranging from 4850 to 124,300 $/incremental ton reduced, according to a 1990 CONCAWE study [8].

9.3.15. Storage tanks

In paragraph 4.21.3 it is mentioned that "a technique to reduce VOC from tanks is to blanket them". It is proposed to replace this sentence by "a technique to reduce VOC emissions is to increase the storage pressure, e.g. by blanketing and raising the set pressure of the overpressure relief device".

10.   CONCLUSIONS

This report documents an evaluation of a number of key available techniques for reduction of air emissions based on collected real plant data. Based on this analysis several amendments are proposed to the Refining BREF, which is subject for review by a Technical Working Group convened by the IPPC Bureau.

The majority of proposed amendments are related to Associated Emission Levels (AELs) for Best Available Techniques (BAT), others mainly cover applicability issues and to a less extent cross-media effects. Importantly differentiation has been made between new units and retrofitting existing facilities as befits the maturity of the European industry.

Unless specified otherwise proposed AELs should only represent normal operations, excluding start-up and shutdown conditions and special short time operations such as steam-air de-coking chemical cleaning of radiant cell tubes or soot blowing of heat transfer surfaces. Consistent with the current BREF proposed AELs should be based on daily averages unless specified otherwise and comprise ranges of values with the position of specific technologies within the ranges identified. In this way there should no longer be very wide ranges assigned to generic techniques.

In some cases the current BREF defines AEL ranges for certain emissions to be achieved by 'a suitable combination of techniques'. In this report it is proposed to eliminate this approach and provide AEL ranges for each technique separately. This will allow a clearer interpretation of BAT.

This study did not set out to gather cost data in view of the highly site specific nature of projects that can greatly multiply manufacturers data and the technical and legal difficulties involved in discussing commercial information. In some instances cost information has come to light in the course of the work. This has been included but has not been subjected to scrutiny.

Data gathered has led us to conclude that some of the AEL ranges in the current BREF do not adequately cover all of the technologies they intend to and we have proposed changes which in some qualified cases lead to an increase in the upper AEL range. Generally there are good reasons for this tied to specific operating constraints. The lower AEL range values are in some cases only achievable under narrow sets of conditions. Support for this view is offered by comparison of the AEL ranges with the recently reviewed US EPA standards (Standards for Petroleum Refineries (40 CFR part 60, subpart J) amended June 24 2008) shown in **Table 10-1**. It can be concluded that the current BREF lower AEL ranges for a number of key techniques are often more stringent compared to the most recent US EPA standards.

Table 10-1 Comparison BAT- US EPA

	BAT AEL (1)	US EPA (1)	Comments
H_2S in fuel gas	20-150 mg/Nm³ daily avg	245 mg/Nm³, 3 hr rolling avg 91 mg/Nm³, 365 day rolling avg	Lower AEL more stringent than US EPA
SO_2 from fuel gas combustion	5-20 mg/Nm³ daily avg	49 mg/Nm³, 3 hr rolling avg 20 mg/Nm³, 365 day rolling avg	Lower AEL more stringent than US EPA
NO_x fired heaters	20-150 mg/Nm³ daily avg applicable to all units	70 mg/Nm³ , 24 hr rolling avg Applicable to > 12 MW	Lower AEL more stringent than US EPA
FCC SO_2	10-350 mg/Nm³ daily avg	122 mg/Nm³, 7 day rolling avg 61 mg/Nm³, 365 day rolling avg	Lower AEL more stringent than US EPA
FCC NO_x	40-150 mg/Nm³ daily avg	140 mg/Nm³, 7 day rolling avg	Lower AEL more stringent than US EPA
FCC PM	10-40 mg/Nm³, daily avg	100 mg/Nm³, for existing unit 50 mg/Nm³ for new units	AEL more stringent than US EPA
SRU	99.5-99.99% sulphur recovery efficiency	713 mg/Nm³ SO_2 in tail gas (is equivalent to +/- 99.9% sulphur recovery efficiency)	BREF and US EPA not consistent

(1) All flue gas concentrations are @ 3% O_2

In the following paragraphs some main conclusions are drawn for each technique which has been investigated.

10.1. NO_X FROM COMBUSTION

Two Best Available Techniques (BAT) have been subject to evaluation: Low NO_x burners and Selective Reduction of NO_x for fired heater and boilers, both non-catalytic (SNCR) and catalytic (SCR).

Analysis of 31 real plant datasets resulted in 24 proposals for amending the BREF.

The main outcome for the Low NO_x burner technique is that overall the current BREF AEL ranges are too optimistic for gas firing applications and far too optimistic for liquid firing heaters and boilers. Increased levels have been proposed, coupled to the majority fuel concept approach for NO_x and PM for dual firing as also defined in the current LCP Directive.

To a large extent operating conditions (fuel quality, preheat temperature) determine where in the range emissions will fall. The BEES approach [11] that parameterises the effects of air preheat, fuel hydrogen content, bridge-wall temperature and fuel nitrogen content has been shown to well explain the range.

For SNCR it is concluded and included in a proposed amendment that only a narrow window of applicability exists. Both for SCR and SNCR broader AEL ranges for the NO_x emission reduction efficiency and also for the ammonia slip from SCR have been proposed.

10.2.   AIR EMISSIONS FROM CATALYTIC CRACKER UNITS

The analysis made for the catalytic cracking process covers a wide range of available techniques to reduce or control SO_2, NO_x, CO and PM emissions: CO Boiler, O_2 control for full burn units, SO_x reducing additives, NO_x reducing additives, Low NO_x CO combustion promoter additives, SNCR, SCR, Wet Gas Scrubbers (WGS), Third Stage Cyclones, Third Stage Backflow Filters and Electrostatic Precipitator (ESP).

Analysis of 37 datasets resulted in over 66 proposals for amending the BREF. Following are the key outcomes of that evaluation:

- The upper end of AEL ranges for the NO_x emission from a CO Boiler and for residual fuel processing does not cover the wide range of existing applications and is therefore proposed to be amended.
- Low NO_x CO Combustion Promoter is widely applied in industry to control NO_x and CO emissions and should be included as a BAT.
- Although NO_x reduction additives have shown a potential in some applications, it has not been proven successful yet in several units and therefore are proposed as an emerging technique.
- The lower AEL of the NO_x reduction efficiency for SNCR has been demonstrated to be too high, while the upper AEL for ammonia slip has been shown to be too low, therefore amendments have been proposed for these AEL ranges.
- SNCR shows to have a narrow window of technical applicability and is even not to be considered BAT for all retrofit cases.
- It is proposed to increase the upper range for ammonia slip in SCR applications.
- It is proposed to add third stage backflow filters as an emerging BAT to control PM emissions.
- It has been concluded to use the outlet PM emission concentration as the most appropriate AEL parameter for ESPs, rather than removal efficiency and furthermore to base the AEL range on monthly averages instead of daily averages to account for specific safety precautions required during start-up and shutdown operations.
- On wet gas scrubbers it is proposed to express performance and AELs in terms of outlet concentration for SO_2, PM and NO_x instead of removal percentage. Amendments have been proposed to increase the upper AEL for PM and to increase the lower AEL for SO_2.

10.3.   AMINE TREATING

This technique is very widely used to remove H_2S from refinery fuel gas streams and consequently its performance is key to the achievable SO_2 emission level from combustion units fired on refinery fuel gas.

Based on a theoretical evaluation and on some real plant data it has been concluded that the upper AEL for H_2S in fuel gas from amine treating and for SO_2

from combustion on refinery fuel gas need to be increased. The upper ranges proposed depend on scrubber pressure and fuel-gas hydrogen content. Furthermore the AEL for SO_2 emissions should be established not only based on the H_2S content of the refinery fuel gases but also account for the potential content of other sulphur species not easily removed.

10.4. SULPHUR RECOVERY UNITS

Sulphur Recovery Units can be a relatively significant source of refinery SO_2 emissions. For that reason CONCAWE requested Sulphur Experts Inc. to carry out an analysis of the sulphur recovery performance of real plant data and also to provide more insight in the relative cost of various techniques and to evaluate the cross-media aspects on associated the CO_2 emission.

Based on the study done by Sulphur Experts Inc. on 114 datasets it has been proposed to replace the current BREF AELs for a number of named techniques by AEL ranges for the overall sulphur recovery efficiency for Claus plants and for three main categories of Tail Gas Clean Up Units. In addition it is proposed to decrease the lower AEL in Chapter 5 for both new and existing units. Finally information is provided on the relative cost and impact on CO_2 emission of several SRU techniques.

10.5. VAPOUR RECOVERY UNITS

Based on the conclusions derived from 7 real plant datasets it is proposed to use the outlet concentration as a prime AEL parameter, rather than the removal efficiency for VOCs (Volatile Organic Compounds), and to base the AEL and the averaging time on the values defined in the Gothenburg Protocol.

For benzene the AEL is proposed to be brought in line with the observed emission level identified in an IP paper [9], resulting in a higher value compared the current BREF AEL.

Finally it is proposed to differentiate between Volatile Organic Compound (VOC) and Non-Methane VOC (NMVOC), and between gasoline service and other streams when it comes to defining AELs for double stage units.

11. REFERENCES

1.   EIPPCB (2003) Integrated Pollution Prevention and Control (IPPC) – reference document on Best Available Techniques for mineral oil and gas refineries. Sevilla: European IPPC Bureau

2.   CONCAWE (1999) Best available techniques to reduce emissions from refineries. Document No. 99/01. Brussels: CONCAWE

3.   CONCAWE (2003) The IPPC directive, refinery BREF, and European refineries – a guidance manual. Report No. 4/03. Brussels: CONCAWE

4.   EIPPCB (2008) Guidance document on improving the collection and submission of data for the review of the BREFs. IEF 20-4. Sevilla: European IPPC Bureau

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6.   Sulphur Experts (2009) Evaluation of sulphur recovery technologies. Project No. SE827B. Calgary AB: Sulphur Experts Inc.

7.   Mastropietro, R.A. (1995) Prevention of fires and explosions in electrostatic precipitators. Somerville NJ: Hamon Research-Cottrell Inc. http://hamon-researchcottrell.com/Prod_Electrostatic.asp

8.   CONCAWE (1990) VOC emissions from gasoline distribution and service stations in Western Europe - control technology and cost-effectiveness. Report No. 90/52. Brussels: CONCAWE

9.   Energy Institute (2004) IP Research Report: An investigation into suitable instruments for the measurement of TOC in emissions from VRUs. London: Energy Institute

10.   EU (2002) Proposal for a Council Decision on the accession, on behalf of the European Community to the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution to abate acidification, eutrophication and ground-level ozone (2002/0035 (CNS) - COM(2002) 44 final). Official Journal of the European Communities No. C151E, 25.06.2002

11.   Ministerie van VROM (1987) Besluit emissie-eisen stookinstallaties milieubeheer A (Bees A). Staatsblad van het Koninkrijk der Nederlanden Stb. 164, 1987

APPENDIX I

NO_x Adjustment Factors to Account For Operational Variables In Combustion Systems

It is well understood that NO_x emissions resulting from the combustion of gaseous and liquid fuels are not only influenced by system design but by operational variables such as fuel mix, fuel composition, combustion air temperature and firebox temperature. In recognition of this and to assist the permitting process, the Dutch Ministry of Environment and the Dutch Ministry of Economic Affairs, developed and incorporated a number of adjustment factors (in the form of correlations) into their "Besluit Emissie-Eissen Stookinstallaties Milieubeheer A" (BEES) guidance document for permitters (April, 1987). These adjustment factors provide very helpful input to the process of establishing a suitable BAT AEL range for primary NO_x abatement technology (i.e. low/ultra-low NO_x burners).
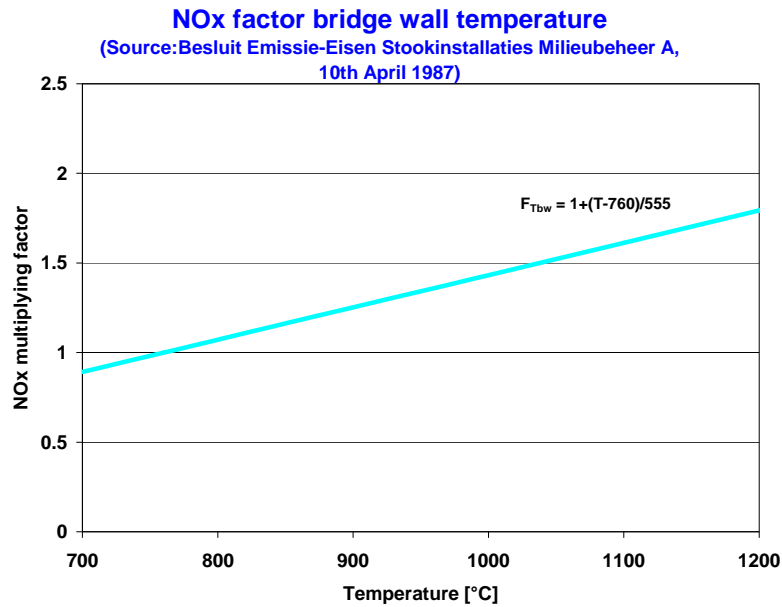
What follows is taken directly from the BEES document and then applied to the data sets discussed in the body of this report (Section 4.1.2.2).

1. The BEES correlation to account for variation in the combustion air preheat temperature.

NOx multiplier for APH
(Source:Besluit Emissie-Eisen Stookinstallaties Milieubeheer A, 10th April 1987)
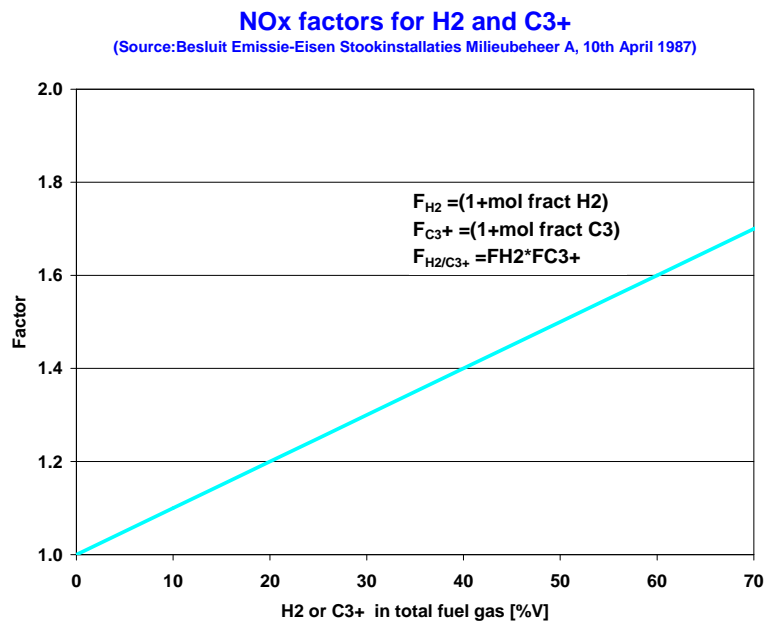

$$F_{APHT} = 1/(1.18-0.0018*(A8+100))$$
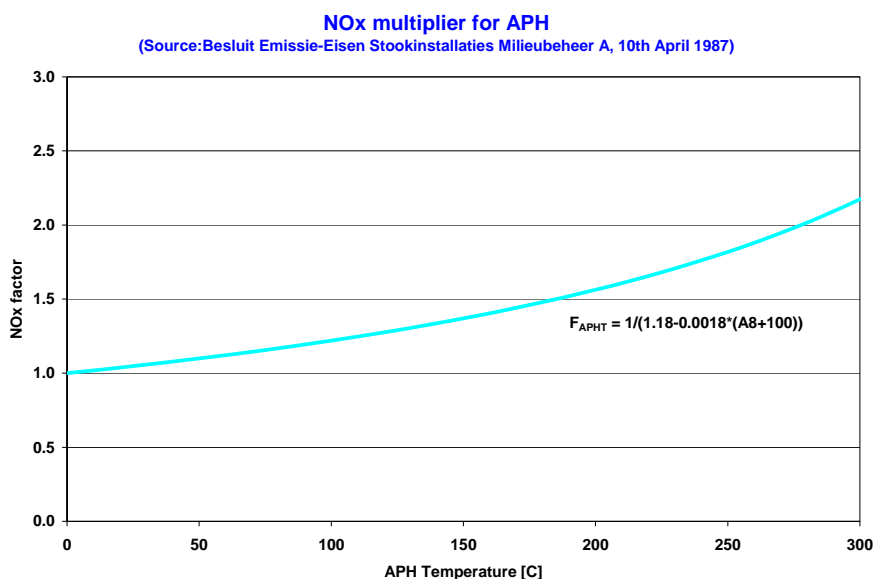
This factor is applied directly for units fired in fuel gas. Because it addresses the increase in thermal NO_x production care must be taken not to double count an increment in prompt NO_x arising from fuel Nitrogen conversion. Therefore, in the case of fuel oil or combination oil and gas firing it is only applied after first adjusting the bound fuel nitrogen to a zero level (using the correlation in section 4) to ensure the factor is applied only to the thermal NO_x component.

2. The BEES correlation to account for variation in the firebox (bridge wall) temperature

NOx factor bridge wall temperature
(Source:Besluit Emissie-Eisen Stookinstallaties Milieubeheer A,
10th April 1987)

$F_{Tbw} = 1+(T-760)/555$

NOx multiplying factor vs *Temperature [°C]*

3. The BEES correlation to account for variation in the refinery gas composition

NOx factors for H2 and C3+
(Source:Besluit Emissie-Eisen Stookinstallaties Milieubeheer A, 10th April 1987)

$F_{H2} = (1+mol\ fract\ H2)$
$F_{C3+} = (1+mol\ fract\ C3)$
$F_{H2/C3+} = FH2*FC3+$

Factor vs *H2 or C3+ in total fuel gas [%V]*

The adjustment factor for refinery fuel gas composition in BEES is made up of a combination of two factors multiplied together. The first accounts for the hydrogen content and the second for hydrocarbons having a carbon number greater than 3 (the C3 plus content).

4. The BEES correlation to account for variation in the bound nitrogen content of the liquid fuel

NOx multiplying factors for bound nitrogen in fuel oil
(Source:Besluit Emissie-Eisen Stookinstallaties Milieubeheer A, 10th April 1987)

$$F_{BN} = 1.76 - 1.41\ e^{\wedge}\ (-2.06*N)$$
where N is in % m/m

Bound Nitrogen [% m/m]

Multiplying factor
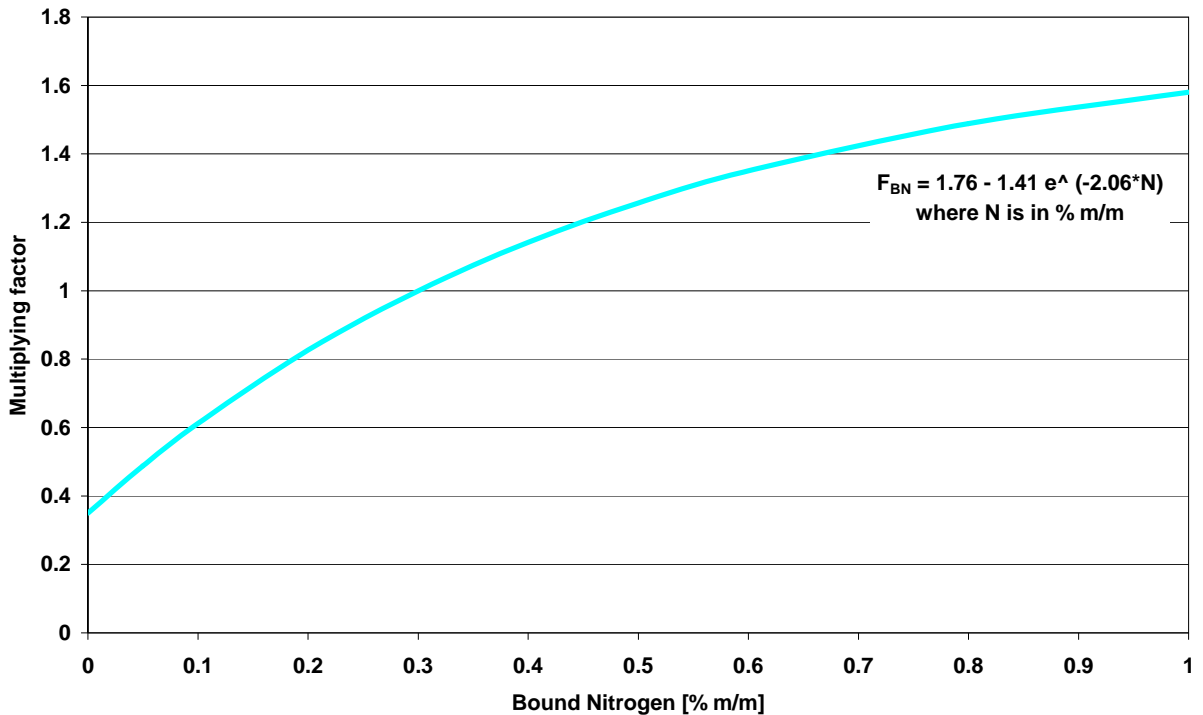
Here the zero bound nitrogen on the curve correspond to the "thermal NO_x component" in the overall NO_x levels derived from fuel oil firing with no combustion air preheat. When using the air preheat factor (see section 1) to adjust NO_x expected levels at higher than ambient temperature, only the "zero bound Nitrogen" component of NO_x from fuel oil firing is used.

In combination firing, the adjustment factors in the above figure must also be weighted for the percent of fuel oil firing. Overall, the adjustment process is undertaken as follows:

For Refinery Fuel Gas Firing:

$$NOx_{(REF)} = NOx_{(measured)} *F_{APHT(REF)}/ F_{APHT(A)} * F_{TBW}/ F_{TBW(A)} *F_{H2/C3+(REF)}/ F_{H2/C3+(REF)} \quad (1)$$

For Dual Fuel Firing:

$$NOx_{(REF)} = NOx_{(A)} * F_{BN(N=0)}/F_{BN(A)} * F_{APHT(REF)}/F_{APHT(A)}*F_{TBW(REF)}/ F_{TBW(A)} +$$
$$NOx_{(A)} * (1-F_{BN(N=0)}/F_{BN(A)}) * F_{BN(REF)}/ F_{BN(A)}*\%Oil_{(REF)}/\%Oil_{(A)} \quad (2)$$
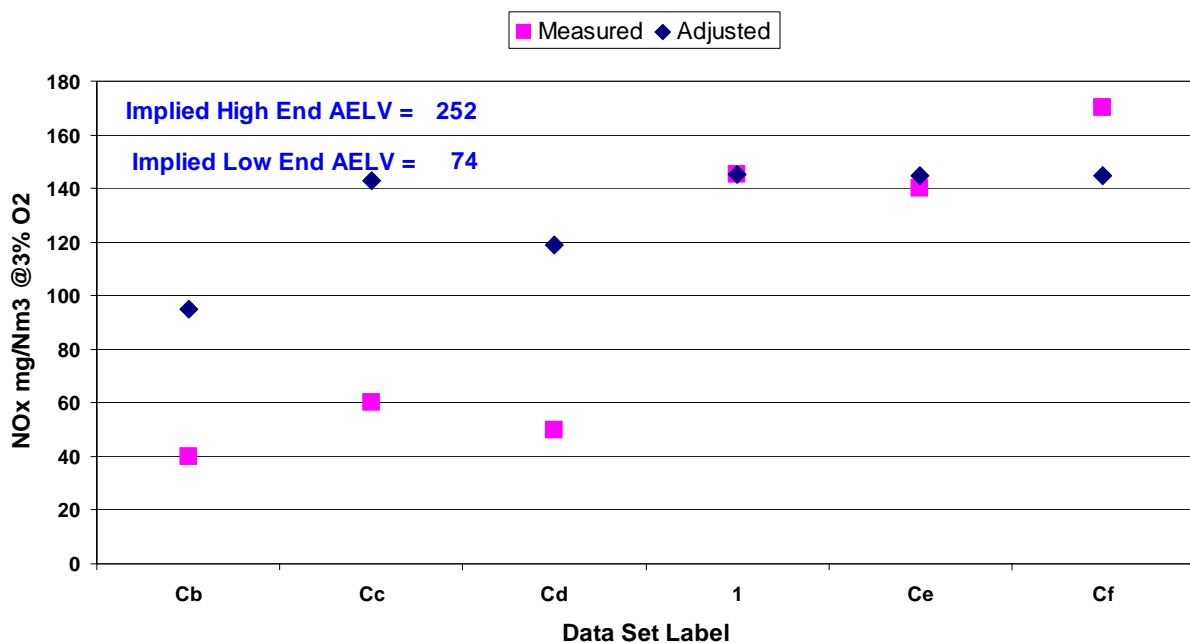
Where (A) = Actual measured values; (REF) = Reference Values.

In each case these adjustment factors, in quantifying the magnitude of the influence of changes in operational variables, serve to highlight their importance and likely influence on achievable NO_x levels in real refinery installations.
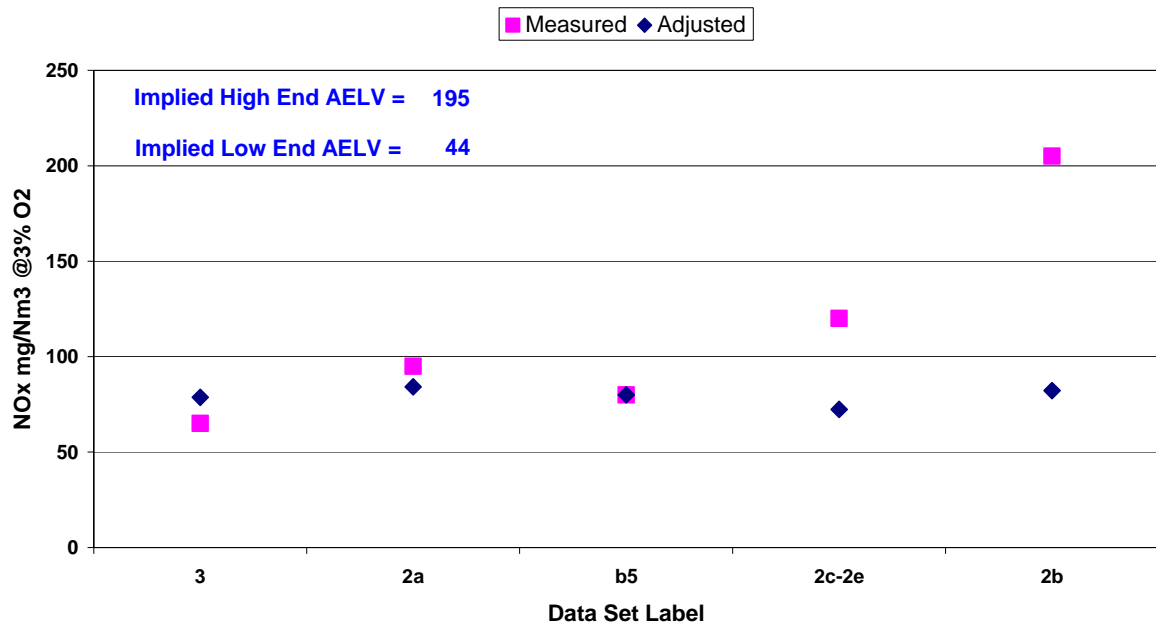
5. Applying the BEES factors to the low NO$_x$ burner data sets in Section 4.1 of this report

To test the influence of the BEES adjustment factors on actual installations, the "median values" of each of the measurement data sets given as **Figures 4**-**1** and **4**-**2** in Section 4.1 were adjusted (using the additional data on air preheat temperature, fuel composition/mix and firebox conditions provided in **Tables 4-1** to **4-4**) to a single set of "reference operating conditions" chosen from a single data set. The results are given below.
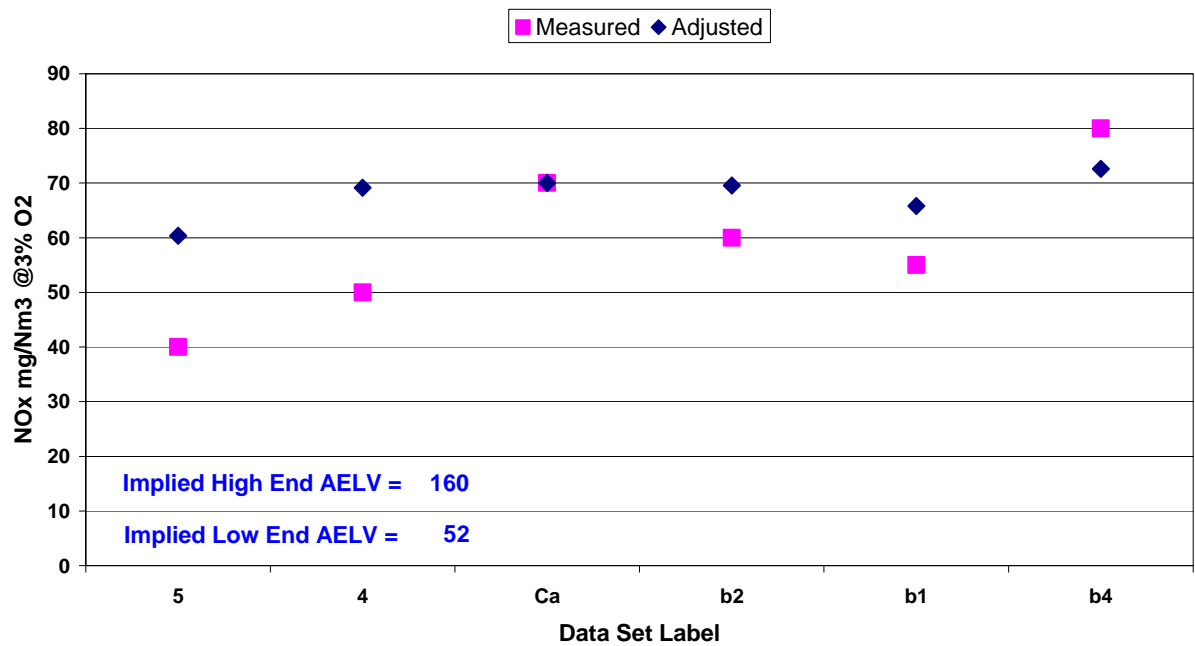
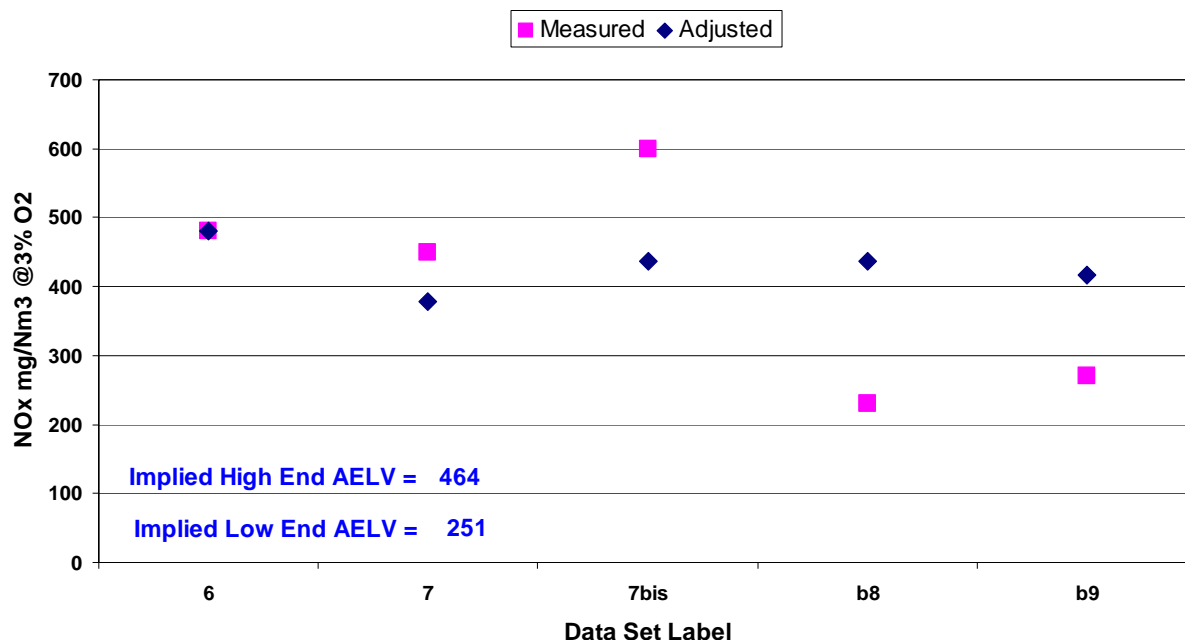### NOx for Staged Air LNB Firing Refinery Fuel Gas

NOx for Staged Fuel LNB Firing Refinery Fuel Gas

■ Measured ◆ Adjusted

Implied High End AELV =   195

Implied Low End AELV =   44

NOx mg/Nm3 @3% O2

Data Set Label

NOx for Ultra Low NOx Burners Firing Refinery Fuel Gas

■ Measured ◆ Adjusted

Implied High End AELV =   160

Implied Low End AELV =   52

NOx mg/Nm3 @3% O2

Data Set Label

NOx for Dual Fired Combustion Units

■ Measured ◆ Adjusted

Implied High End AELV =   464

Implied Low End AELV =   251

The first observation in comparing the "unadjusted" data with the "adjusted data" is that compensating for variations in the key operating variable, within a given technology type, largely accounts for the variations in NO_x emissions (at least when using the median data). This both affirms the general robustness of the BEES factors and enables some general conclusions to be reached over the implications of the data sets themselves.

Inevitably the data sets are limited and cannot cover the whole spectrum of expected operations. Confirmation of the ability to consistently adjust the actual measured data to another set of operational conditions significantly assists in the process of robustly assessing the BAT AEL range to account for this spectrum.

This process was undertaken to generate what appears as "Implied High End" and "Implied Low End" AELV which appear on each of the charts. For example, the low end assumption for the combustion air temperature is "ambient", the "high end" assumption is 300°C for gas firing and 200°C for oil firing. In the case of combination firing, the "high end" assumption for bound nitrogen is 0.5% and the low end 0.2% assuming, in each case a 50% oil to total firing ratio is assumed.