# Process Design Technical Note

# TECHNICAL NOTE

## SPECIFICATION OF SCRUBBER OUTLET CONCENTRATIONS

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## 1. INTRODUCTION

In order to comply with the requirements of Integrated Pollution Control (IPC) potential discharges to the environment need to be prevented, minimised and rendered harmless. Progressively from March 2003 Integrated Pollution Prevention and Control (IPPC) permits will be introduced to the organic chemicals industry, replacing IPC Authorisations. This will require the Best Available Techniques to have been systematically applied to control environmental impacts from industrial activities.

The best technique for many potential pollutants is to scrub with appropriate liquids.

This technique is most suitable for chemicals that can be reacted to form a relatively harmless product by fast chemical reaction requiring relatively short contact time with the absorbent, particularly acid and alkaline gases or vapours.

In specifying a scrubbing system / method the most important parameter is the discharge quantity and concentration of the pollutant. This needs to be acceptable from two aspects; health and safety and environmental, although these are rapidly becoming one and the same thing. Therein lies the current difficulty and uncertainty.

There are a number of guidelines and/or limits, recommended or mandatory, covering this subject that are sometimes un-related and inconsistent.

This note is an attempt to describe the various factors that have to be reconciled by scrubber discharges to atmosphere.

## 2. RELEVANT STANDARDS

### 2.1 Control of Substances Hazardous to Health Regulations 1999 (COSHH)

The COSHH Regulations are issued under the umbrella of the Health and Safety at Work etc Act 1974. They define substances hazardous to health and lay down a step-by-step approach for employers to protect workers from risks to their health from hazardous substances.

Two types of occupational exposure limits for hazardous substances are set by HSE and are published annually in the document EH40, EH40/2002 being the latest. These are

OES – Occupational exposure standard and
MEL – Maximum exposure limit.

Both types of limit are concentrations of hazardous substances in the air, averaged over a specified period of time referred to as a time weighted average (TWA). Two time periods are used

| | | |
|---|---|---|
| long-term (LTEL) | 8 hours | *Concentrations are expressed* |
| short-term (STEL) | 15 minutes | *at 1 atmosphere and 20$^{o}$C.* |

An OES is set at a level at which there is no current indication of a risk to the health workers exposed to it by inhalation day after day. However, the environment and persons outside the workplace could well be exposed to the OES level for periods longer than 8 hours with consequent effects.

A MEL is set for substances which may cause more serious health effects and for which ‘safe’ levels of exposure cannot be determined.

## 2.2 Environment Agency – IPC and IPPC

The IPC Regulations have now been superseded legally by IPPC for new processes.

The conditions and any limits to emissions under IPPC are currently under consultation will be announced once European-wide Technical Notes (BREF Documents) have been written and issued.

The Benchmark figures quoted in the Draft Sector Guidance Note IPPC S4.02 "Guidance for Speciality Organic Chemicals" (16.09.2002) have been used as the current reference document.

### 2.2.1 IPC Technical Guidance Notes

The IPPC Sectorl Guidance Notes issued by the Environment Agency will set out Benchmark release levels for emissions to air for a number of named pollutants in particular and VOCs in general. The release levels given are applicable to each non-combustion point source and are reckoned to be achievable by new processes using the best available techniques.

However, they should not be applied as uniform release limits, but should be assessed to take account of site-specific conditions so as to comply with the requirement to use BAT and any relevant environmental quality standards.

*Concentrations are expressed at 1 atmosphere and 0$^{o}$C.*

### 2.2.2 Environment Agency – Technical Guidance Note E1

**"Best Practicable Environmental Option Assessments for IPC"**

The Guidance Note sets out a methodology for assessing harm and comparing options to determine BATNEEC having regard to BPEO. This BPEO appraisal method is not compulsory for IPC Applications, but it is an indicator of the likely future requirements for IPPC.

IPC requires that BATNEEC is used to prevent or minimise releases of prescribed substances and to render harmless any substances which are released.

In addition, there is a implicit requirement that any emission be free from odour at the site boundary.

**Environmental Quality Standards (EQS)**

The EA has a duty to specify conditions in IPC Authorisations to ensure compliance with EC Mandatory Environmental Quality Standards (EQS). It is proposed to limit the concentration of emissions to the EQS level, as a maximum. EQSs exist for only a limited number of substances, the most relevant one being sulphur dioxide.

Typical background levels for $SO_2$ in mg/m$^3$ are

| | | | |
|---|---|---|---|
| Major city | 0.16 | Developed urban | 0.12 |
| Urban in rural setting | 0.10 | Partially developed | 0.07 |
| Rural 0.05 | | | |

*2.2.2 Environment Agency – Technical Guidance Note E1 (Cont.)*

### Environmental Assessment Levels (EAL)

Environmental harm is judged by considering the environmental concentration of a substance in comparison to a reference level for that substance. The EA defines this reference level as the EAL, expressing the relative potential for harm of the substance.
Provisional EALs for each environmental medium are listed in E1 for a wide range of substances. In many cases both short-term and long-term EALs are given.

### Priority for Control

Mechanisms have been developed to determine whether a substance should be a "priority for control" i.e. further reduction, or considered environmentally insignificant.

If the Predicted Environmental Concentration (PEC), including the Process Contribution (PC), resulting from the release is high compared to the EAL, or the PC alone is more than a small fraction of the EAL, the emission is considered to be a priority for control.
The concentrations are the maximum ground level concentration for emissions to air.

| | |
|---|---|
| These limits are defined as | $PEC \geq 0.8\ EAL$ |
| or | $PC \geq 0.02\ EAL$ |
| Releases are considered insignificant if | $PC \leq 0.002\ EAL$ |
| The relationship between PEC and PC is given by where B is the background concentration. | $B + PC = PEC$ |

The figures have been set by "rule of thumb".

## 2.2.3 HMIP Technical Guidance Note (Dispersion) D1

**"Guidelines on discharge stack heights for polluting emissions".**

The Guidance Note sets out a methodology for the determination of discharge stack heights for polluting emissions.

The stack height is determined from the following variables:-

Total volume flow of discharge, pollutant flowrate, emission temperature, pollutant Pollution Index.

The Pollution Index is determined from the Guideline concentration of the pollutant, defined as the concentration to which the general public may be safely exposed for continuous periods of between about 5 minutes and an hour, which may be repeated intermittently but probably infrequently in the long term (10% of the time at most).

If a Guideline is not available the level commonly used is 1/40th of the STEL of the OES, or, if STEL is not available, 1/40th of LTEL of the OES.

*Concentrations are expressed at 1 atmosphere and 20$^{o}$C.*

## 3. DESIGN CRITERIA

The two main criteria to satisfy in specifying the exit concentration of a pollutant from a scrubbing system are;

1. the exit concentration of the pollutant

and

2. the resultant ground level concentration of the pollutant.

The latter figure depends on the height of the vent stack, the efflux velocity and the duration of the discharge.

If the concentration of the pollutant leaving the stack is at or below the long term OES or MEL then there will be no COSHH implications.

However, there may still be environmental implications as the EAL is based generally on a fraction the EH40/95 OEL values.

### 3.1 Application to Common pollutants

For illustrative purposes, a number of major pollutants are considered and the data in the Table 3.1, overpage, is applicable.

## 4. RECOMMENDED DESIGN STEPS

1. The scrubber exit concentration should be less than the lower value of the IPC Benchmark release level **or** the OES (LTEL) for each pollutant.

   This will satisfy the current legislative requirements for IPC and cover the COSHH situation of people working adjacent to a stack being exposed to emissions (e.g. stack sampling).

   Set the scrubber exit concentrations to the following **maximum** values i.e. 75% of lower of IPC Benchmark release levels and OES (LTEL).

   These values will provide a safety factor in the design that will certainly satisfy BAT.

## Table 3.1 Concentration of Pollutants: Guidelines

**All concentrations in mg/m$^3$**

| | At Ground level | | | | | | | At emission point | |
|---|---|---|---|---|---|---|---|---|---|
| | OES [1] | | EQS [2] | EAL [2] | | D1 [3] Guideline concentration | Low Odour Threshold [4] | IPPC [5] | design target |
| | STEL | LTEL | | STEL | LTEL | | | | |
| $CO_2$ | 27400 | 9150 | | - | - | - | - | - | - |
| $NO_2$ | 9.6 | 5.7 | 0.2 [7] | 0.286 | 0.04 | 0.1 | 2.0 | 200 | 4.3 |
| NO [11] | 44 | 31 | | 4.5 | 0.3 | | 0.35 | 130 [5.1] | 23 |
| $SO_2$ | 13 | 5.3 | 0.12 [7] | 0.37 [8] | 0.12 [9] | 0.44 | 1.2 | 50 [5.2] | 4.0 |
| $SO_3$ | - | 1 [10] | | - | - | - | 1 [10] | 62.5 | 0.75 |
| $NH_3$ | 25 | 18 | | 2.4 | 0.17 | 0.63 | 0.03 | 10 | 7.5 |
| HCl | 8 | 2 | | 0.7 | 0.007 | 0.10 | 7.0 | 10 | 1.5 |
| HBr | 10 | - | | 1.0 | - | - | 6.7 | 5 | 3.8 |
| HCN | 11 | - | | 0.2 | - | - | 0.9 | 2 | 1.5 |
| $Cl_2$ | 2.9 | 1.5 | | 0.3 | 0.015 | - | 0.03 | 10 | 1.1 |
| $Br_2$ | 2.0 | 0.66 | | 0.2 | 0.007 | - | 0.33 | 10 | 0.5 |
| $H_2S$ | 14 | 7 | | 0.15 | 0.14 | - | 0.0007 | 5 | 3.8 |
| trimethylamine | 37 | 25 | | 3.6 | 0.24 | | 0.0008 | 2 | 1.5 |
| triethylamine | 63 | 42 | | 6.0 | 0.4 | - | 0.36 | 22 [5.3] | 17 |
| monomethylamine | - | 13 | | 3.6 | 0.12 | - | 0.025 | 7 [5.3] | 5 |
| acetic acid | 37 | 25 | | 3.7 | 0.25 | - | 2.5 | 52 [5.4] | 19 |

[1] As defined by EH40/2002

[2] As defined in E1 Third impression 1998.
In general; short-term EAL = short-term OES / 10
long-term EAL = long-term OES /100

[3] As defined in HMIP Technical Guidance Note (Dispersion) D1, "Guidelines on discharge stack heights for polluting emissions".

[4] As defined by Ruth, J. H., "Odor Thresholds and Irritation Levels of Several Chemical Substances", Am.Ind Hyg.Assoc.J. (47), March 1986.

[5] As defined in IPPC Draft Sector Guidance Notes, IPPC S4.02
[5.1] NO: equivalent to 200mg/m$^3$ $NO_2$
[5.2] $SO_2$ by wet scrubbing
[5.3] triethylamine, monomethylamine: equivalent to dimethylamine
(Benchmark is 10 mg/m$^3$ ***total amine*** as DMA)
[5.4] Acetic acid: equivalent to 80mg/m$^3$ of toluene (VOC Class B)

[6] median of daily mean with ≤ 40 µg/m$^3$ particulates

[7] set by expert Air Quality panel, 15 minute reference period

[8] based on U.S. EPA data

[9] EAL = EQS

[10] As sulphuric acid

[11] Reacts instantly with air to give $NO_2$

*4. Recommended Design Steps **Cont.)***

2. For the minimum discharge stack height of 3m above the building peak height, calculate the maximum ground level concentration of the pollutant.

   If the maximum ground level is less than the lower of the long-term EAL or Low Odour Threshold, then the design is acceptable.

   (*should be <=0.02EAL, insignificant if <= 0.002 EAL)*

   If the maximum ground level is more than the lower of the long-term EAL or Low Odour Threshold the design is unacceptable.

   Then, either

   an iterative design on the scrubber has to be performed until the maximum ground level is less than the lower of the long-term EAL or Low Odour Threshold for the existing vent stack

   or, an iterative design on the stack height has to be performed until the maximum ground level is less than the lower of the long-term EAL or Low Odour Threshold for the existing scrubber exit concentration.

3. A balance will need to be struck between the specification of the scrubber and the stack height. This will require an economic and / or policy decision for the particular set of circumstances for the problem under consideration.

4. For Batch Processes, towards which this Note is mainly directed, the emissions to and from a scrubbing system are generally intermittent and of relatively short duration. (A typical reaction leading to the generation of pollutants will generally be within a period of 1 to 4 hours).

   This is where the concept of TWA becomes relevant (see Appendix 1.1 for definition).

   By following the foregoing design method a very conservative design specification will be generated for intermittent emissions that calculation of TWA ground level concentrations of pollutants will confirm.

5. The design so far has been to specify the outlet conditions for a single scrubber performing the duty.

   Finally, it is essential to determine the desirability or necessity of a back-up scrubber. This will require an economic and / or policy decision for the particular set of circumstances for the problem under consideration.

## Appendix 1. Calculations and Conversions (EH40 Method)

### 1.1 Calculation of concentrations with regard to a specified reference period

#### The 8-hour reference period

The term '8-hour reference period relates to the procedure whereby the occupational exposures in any 24-hour period are treated as the equivalent to a single uniform exposure for 8 hours (the 8 hour time-weighted average (TWA) exposure)

$$\text{The 8-hour TWA} = \frac{C_1T_1 + C_2T_2 + \ldots C_nT_n}{8}$$

where $C_1$ is the occupational exposure and $T_1$ is the associated exposure time in hours in any 24-hour period.

### Example

An operator works near an emission source emitting 10 of ammonia for 6hrs 30 minutes ( Note: this is above the recommended design limit for a scrubber).

$$\text{The 8-hour TWA is} \quad \frac{(6.5 \times 10) + (1.5 \times 0)}{8} = 8.13 \text{ mg/m}^3$$

### The short-term reference period

Exposure is recorded as the average over the specified reference period, normally 15 minutes. For emissions less than the reference period exposure should not exceed **three times the short-term limit.**

### 1.2 Conversion of concentrations in ppm to mg/m$^3$

$$\text{Concentration in mg/m}^3 = \frac{\text{concentration in ppm x MW x 273}}{22.41 \text{ x reference T } (^oK)}$$

where 22.41 l/mol is molar volume of an ideal gas at 0$^o$C and 1 atmosphere

#### Example

For 20$^o$C reference temperature

$$\text{mg/m}^3 = \frac{\text{ppm x MW}}{24.06}$$

For 0$^o$C reference temperature

$$\text{mg/m}^3 = \frac{\text{ppm x MW}}{22.41}$$