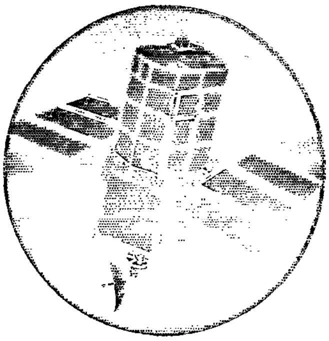
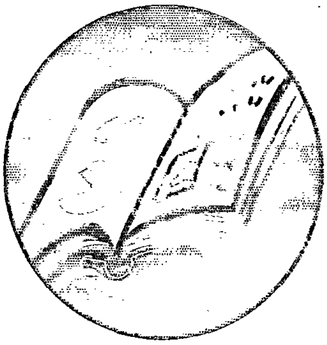
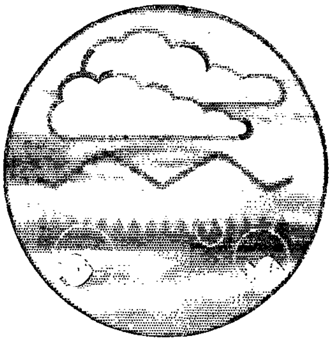
Best Available Techniques for the Control of Pollution in Petrochemicals and Large Volume Organic Chemical Processes







Research and Development

Technical Report
P181

ENVIRONMENT AGENCY

Best Available Techniques for the Control of Pollution in Petrochemicals and Large Volume Organic Chemical Processes

R&D Technical Report P181

Research Contractor:

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Statement of use
This report provides information on best available techniques for pollution control in petrochemical and large volume organic processes. It includes costs of the techniques and economic information on the industry sub sectors. The report will be used in the revision of IPC process guidance on the relevant process.

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EXECUTIVE SUMMARY

The information presented in this report is intended to inform the revision of Integrated Pollution Control Guidance Notes for two categories of process: petrochemicals and large volume organic compounds.

The following topics are reviewed in the report:

- type and sources of pollution from petrochemical and large volume organic plants, and typical methods of abatement in the UK

- available techniques for abatement of pollution from petrochemical and large volume organic compound processes, and their use internationally

- economic background to the producer industry and the implications of costs of abatement.

Suggestions are given in the table overleaf of generic techniques and criteria that are suggested as BAT, based on the research performed. The focus is on organic compounds as being most characteristic of these processes. Minimisation of pollution, and internal recycling, are preferred methods of abatement and these are shown on the table as general principles.

One possibility identified in the report is that the cost per ton of VOC abated might provide a useful context to Inspectors. A method of calculating annualised cost and indicative ranges of values are contained in the body of the report.

A further point of note relates to aqueous effluents, where the treatment plant is often outside the limit of the authorised process. It is suggested that any effluent from process plants should be treatable by conventional wastewater treatment to an acceptable level, but this has not been quantified.

The economic analysis demonstrates the cyclical nature of the business for many plants in the category of petrochemicals and large volume organics. Costs of abatement are put into the context of industry economics. It is recommended that, where possible, the costs of abatement are related to the economics of individual products and processes rather than of companies. The analysis in this area is only broadly indicative.

Table 1 Good practice: suggested techniques and principles

Type and source of pollution	Abatement technique
VOCs to air	
Storage tanks: volatile liquids	Internal or external floating roof tanks *or* fixed roof tanks to recovery or destruction Overfill prevention: level measurement and alarms, preferably auto cut-off
Transfer of volatile liquids	Vapour balance lines Bottom filling road/rail tankers Any net vapour displacement to recovery or destruction; maximum $35 g/m^3$ outlet for VOCs (total)
Controllable vents	Abatement to achievable release concentrations for non-trivial quantities; with consideration of cost effectiveness?
Fugitive emissions	Leak detection and repair programme on equipment and fittings handling gases and light organics Progressive installation (to an agreed programme) of high integrity equipment on duties where VOCs of 'high' and 'medium' environmental impact (Class A) are handled
Intermittent emissions	All occasional vents (safety, maintenance etc.) ducted to storage/recycle or to destructive device such as flare
All VOC emissions	Minimisation at source by measures such as closed process systems, high selectivity processes, recycle or fuel use of purge streams
Aqueous effluents	Treatment at the process plant of effluents to a quality that may be adequately treated by conventional water treatment plant
Ground protection	Sealing of ground with impermeable layer where spills or leaks may occur e.g. tank bunds
Landwastes	Minimisation by process design or by recovery and re-use

KEY WORDS AND PHRASES

BAT
Petrochemicals
Organics
Pollution control
Cost of control
Industry economics

1. INTRODUCTION

1.1 Background

In order to assist its Inspectors in the authorisation and regulation of processes prescribed for pollution control, Her Majesty's Inspectorate of Pollution (HMIP) published Chief Inspector's Process Guidance Notes. There is a commitment to the revision of these Notes no later than four years after their publication. Under the Environment Agency, these Notes are known as Integrated Pollution Control Guidance Notes (IPCGNs).

This research report will inform the process of revision of Guidance Notes for two categories of process: petrochemicals and large volume organic compounds. These processes fall into the categories defined in Sections 4.1 and 4.2 of the Environmental Protection (Prescribed Processes and Substances) Regulations SI 1991, No. 427 as amended. Small scale or batch processes falling into the same categories are covered by a separate research report.

In the original Notes, the petrochemicals and large volume organic processes were covered in separate notes: IPR 4/1 to IPR 4/4 and IPR 4/6. It is intended to combine these into a single Note.

Chem Systems has been engaged by the Environment Agency to prepare this research report and, as a separate activity, to assist in drafting the new Note.

1.2 Objectives

The aims of the report are to:

- review the Best Available Techniques (BAT) for the control of pollution from the specified processes, and their cost
- provide an economic assessment of relevant parts of the industry.

In particular, there is a need to consider international practice, not only UK practice. The report must also provide information that will assist Inspectors in determining whether particular techniques entail excessive cost in the context of sector economics.

1.3 Outline scope

The category of petrochemicals and large volume organic compounds covers a wide variety of process types. In addressing the scope, attention has been paid in particular to types of release and abatement techniques that are relevant for a large number of processes. A selected number of processes have also been chosen to indicate the nature of process-specific solutions that may be adopted.

The elements of scope addressed in the report are as follows:

- Current processes and practices in the UK are reviewed in Section 3, indicating the processes included in the scope, characteristic types and quantities of release, and the abatement techniques used. From this, the focus for subsequent work is identified.

- Abatement techniques in use internationally are listed in Section 4, and notes are given of their use on the subject processes. Around 25 of these techniques and variants are analysed in greater detail, with information where available on typical costs and performance.

- Process-specific issues are addressed for six processes. These are either particularly commercially important or have pollution abatement needs that are not adequately described by generic release types or abatement techniques.

- Economic factors are reviewed for six cases, each of which represents either a category of process or a single process of interest. The industry economics and an indicative cost of pollution control are reviewed for each.

2. METHODOLOGY

2.1 General

The sources of information and the analytical methods used in compiling the report are summarised below.

2.2 Current UK Practice

An assessment is provided in the report of the sources of pollution from the processes and of the abatement techniques in use in the UK. The prime source of this information is IPC applications and authorisations for selected plants. The results obtained are indicative but not necessarily statistically representative nor absolutely current.

The documentation for each plant was summarised on a single worksheet using a proforma to assist structuring of the analysis. The summaries are internal working documents from which conclusions are presented in tabular form in the report.

From this review, Chem Systems identified the most common sources of pollution and abatement requirements, to provide a focus for the BAT review.

2.3 Best Available Technique Review

Technical literature and published information from technology suppliers was used to prepare a list of around 150 types of abatement technique that could be applicable to the subject processes and the identified sources of pollution. Interviews were then conducted with West European producers, particularly those who are known either to produce in different continents or have a reputation for advanced pollution control. Where particularly relevant, and where information was not available from other sources, Chem Systems also interviewed selected technology vendors. The results are tabulated in Section 4 of the report, identifying processes or producers where the use of the techniques has been identified.

A more detailed review is made of techniques of particular interest. The emphasis in this analysis is on techniques that go beyond universal good practice. Technical performance and limitations are noted, and the costs of abatement are calculated for several of the techniques studied for typical cases. The capital cost data are usually provided from published sources or vendors, because producers do not necessarily split these costs out from plant investment. The annualised incremental costs are calculated with a capital charge of around 16.25 percent per year, equating to ten percent per annum and a ten year period. In additional to variable costs such as fuel, an allowance is made for maintenance and insurance, but not usually for additional labour or overheads.

In addition to the evaluation of generic techniques, pollution abatement on six processes is reviewed in further detail, once more by interview with industry sources. The processes are selected because they have specific abatement issues or are representative of certain types of operation.

2.4 Economic analysis of the industry

Six processes, or groups of processes, were selected to demonstrate the economics of certain sectors of the petrochemical and large scale organics industries.

Chem Systems runs a continuing programme called Petroleum and Petrochemical Economics (PPE), in which the production economics and profitability of key production processes are analysed quarterly. Business background, including structure of the producer industry and trends in supply and consumption, also are reviewed in the PPE programme and in single client work by Chem Systems. In-house data are therefore used by the consultants in the illustrative analyses of industry economics. The PPE programme covers most of the major commodity petrochemicals and polymers. Data for other processes reviewed in the report are less detailed.

The thrust of the analysis is to place the approximate abatement costs into the context of the costs of production and margins of production processes. For several of the processes, the concept of cyclicality of the business is very important.

3. UK PROCESSES AND PRACTICES

3.1 General

The purpose of this section of the report is to provide and indication of the types and sources of pollution arising from UK petrochemical and large scale organics plants, and the abatement techniques used.

IPC authorisations and applications have been used as the basis of this analysis. While this documentation provides a useful directional overview, it must be recognised that it does not necessarily correspond exactly to current practice.

3.2 Production Processes

The processes covered in this report are petrochemicals and large scale organics. These are taken as the processes shown on Table 3.1. The processes are arranged into five groups: Petrochemicals, Acids and Aldehydes, Sulphur Compounds, Nitrogen Compounds, Monomers and Polymers.

Table 3.1 Petrochemical and Large Volume Organic Compound Processes

Petrochemicals	Acids and Aldehydes	Sulphur Compounds
Butadiene	Acetic acid	Carbon disulphide
Cumene	Acetylene	Dithiocarbamates
Ethanol	Acetic anhydride	Thiols
Ethylbenzene	Adipic acid	Thiophene
Ethylene/ Propylene	Formaldehyde	Ethyl PCT
Ethylene glycol	Formic acid	Viscose fibre
Ethylene oxide	Maleic anhydride	Cellophane and products
Higher olefins	Methacrylic acid	
Isopropyl alcohol	Phthalic anhydride	
Oxo alcohols	Propionic acid	
Vinyl acetate monomer	Terephthalic acid	
Vinyl acetate trimer		

Nitrogen Compounds	Monomers and Polymers
Aniline	Ethylene dichloride (EDC)
Cyclohexylamine	Vinyl chloride monomer (VCM)
Mercaptobenzothiazole	Polyvinyl chloride (PVC)
Methylamine	Styrene
Aminoethanols	Polystyrene
Dimethylcyclohexylamine	Methyl methacrylate (MMA)
Dimethyl-formamide	Polymethyl methacrylate resins
Dimethyl-acetamide	Nylon salt
Choline chloride	Nylon polymers
Quaternary ammonium salts	Polyacrylonitrile fibre (PAN)
Ethylamines/ Isopropylamines	Nitrile butadiene rubber (NBR)
Ethanolamines	Low Density Polyethylene (LDPE)
Acrylonitrile	High Density Polyethylene (HDPE)
Adiponitrile	Linear Low Density Polyethylene (LLDPE)
Hexamethylene diamine	Polypropylene
Hexamethylene tetramine	Polyester/Alkyd resins
Acrylamide	Epoxy resins
Pyridines and their derivatives	Rosin-based resins
	Polyamide resins
	Amino resins
	Phenolic resins

Tables 3.2 - 3.6 give the number of plants in the UK manufacturing the chemicals in the process groups listed in Table 3.1 above. The data in the tables are taken from the Environment Agency database, Chem Systems' in-house company databases and from published directories. The differentiation between "large", "medium" and "small" is not exact. Large plants would typically produce at least 50 000 tons per year or have 200 or more total employees. Small plants would typically produce under 10 000 tons per year or employ fewer than 50 people. Most plants fall into the large or medium category by the nature of the process groups reviewed. Where data are not available, Chem Systems has made a judgement from experience of the industry.

There are very many fewer plants falling into the petrochemical and large volume organic categories than are covered by Sections 4.1 and 4.2 of the Regulations. Smaller scale processes, including many batch operations, are covered by a separate research report.

Table 3.2 Number of Plants Manufacturing Petrochemicals in the UK, 1996

Petrochemicals	**Total Plants**	**Large**	**Medium**	**Small**
Butadiene	**2**	2		
Cumene	**1**	1		
Ethanol	**3**	3		
Ethylbenzene	**2**	1	1	
Ethylene	**5**	5		
Propylene	**12**	10	2	
Ethylene glycol	**1**	1		
Ethylene oxide	**1**	1		
Higher olefins	**1**	1		
Isopropyl alcohol	**2**	2		
Oxo alcohols	**2**		2	
Vinyl acetate monomer	**1**	1		
Vinyl acetate trimer	**1**	1		
TOTAL	**33**	**28**	**5**	

Table 3.3 Number of Plants Manufacturing Nitrogen Compounds in the UK

Nitrogen Compounds	Total Plants	Large	Medium	Small
Aniline	**1**	1		
Cyclohexylamine	**1**	1		
Methylamines	**1**		1	
Aminoethanols	**1**		1	
Dimethylcyclohexylamine	**0**			
Dimethylformamide	**1**		1	
Dimethylacetamide	**1**		1	
Choline chloride	**2**	1	1	
Quaternary ammonium salts	**2**	1	1	
Ethylamines/isopropylamines	**1**	1		
Ethanolamines	**1**		1	
Nitriles and derivatives				
Acrylonitrile	**1**	1		
Adiponitrile	**1**	1		
Hexamethylene diamine	**2**	2		
Hexamethylene tetramine	**1**			1
Acrylamide	**1**		1	
Pyridine/Methyl pyridine/ Demethyl pyridine	**1**			1
TOTAL	**19**	**9**	**8**	**2**

Table 3.4 Number of Plants Manufacturing Acids and Aldehydes in the UK

Acids and Aldehydes	Total Plants	Large	Medium	Small
Acetic acid	**1**	1		
Acetylene	**1**	1		
Acetic anhydride	**2**	2		
Adipic acid	**1**	1		
Formaldehyde	**9**	4	3	2
Formic acid	**1**	1		
Maleic anhydride	**0**			
Methacrylic acid	**1**	1		
Phthalic anhydride	**3**	1	1	1
Propionic acid	**1**		1	
Terephthalic acid	**1**	1		
TOTAL	**21**	**13**	**5**	**3**

Table 3.5 Number of Plants Manufacturing Sulphur Compounds in the UK

Sulphur Compounds	Total Plants	Large	Medium	Small
Carbon disulphide	**1**	1		
Dithiocarbamates	**0**			
Thiols	**0**			
Thiophene	**1**	1		
Ethyl PCT	**1**	1		
Mercaptobenzothiazole	**2**	1	1	
Viscose	**1**	1		
TOTAL	**5**	**4**	**1**	

Table 3.6 Number of Plants Manufacturing Monomers and Polymers in the UK

Monomers and Polymers	Total Plants	Large	Medium	Small
Ethylene Dichloride (EDC)	**4**	4		
Vinyl Chloride Monomer (VCM)	**2**	2		
Polyvinyl Chloride (PVC)	**4**	3	1	
Styrene	**2**	2		
Polystyrene	**5**	4	1	
Methyl Methacrylate	**1**	1		
Polymethyl Methacrylate resins	**8**	4	3	1
Nylon polymers	**2**		1	1
Polyacrylonitrile fibre (PAN)	**1**		1	
Nitrile butadiene rubber (NBR)	**1**		1	
LDPE	**2**	2		
HDPE	**1**	1		
LLDPE	**1**	1		
Polypropylene	**2**	2		
Resins				
Polyester/Alkyd Resins	**13**	2	6	5
Epoxy Resins	**7**	1	2	4
Rosin-based Resins	**1**		1	
Polyamide Resins	**5**	2	2	1
Amino Resins	**1**		1	
Phenolic Resins	**7**	2	3	2
TOTAL	**69**	**32**	**23**	**14**

3.3. Types of Releases

3.3.1. Types and Sources of Release by Process Group

Analysis of the release sources, release types and typical release quantities has been carried out for a selection of the chemical processes in each of the five process groups described in Section 3.2.

For each of the selected chemical processes, copies of the authorisation and applications were obtained from the Environment Agency. The detailed information contained within the documents was summarised into a summary sheet, showing the emission sources and the emission control techniques. These are internal working documents; not included in report.

The summary sheets were used to create three tables for each of the process groups, showing the types of releases to air, water and land for each of the chemical processes. The results are given in Tables 3.7 - 3.21 below.

The information presented here is illustrative and is not necessarily statistically representative of the current situation.

Table 3.7 Petrochemical processes: types of release to air

	Release Source	CO_2	CO	SOx	NOx	VOC	Part[1]	Other
CUMENE								
Tanks & Loading	Storage Tank Breathers		Y	Y		Y		
Continuous Vents	Main Stack, Flare Stack	Y	Y	Y	Y			Benzene, Propylene, Propane, Inerts,
Intermittent Vents	Thermal Relief Valves	Y	Y	Y				
Water Systems	Drain System		Y	Y				Propylene
Fugitive Emissions	Valves/Flanges					Y		
Typical Release Quantity	***% of Total Throughput***	-	-	-	-		-	-
ETHANOL								
Tanks & Loading	Storage Tank Breathers					Y		Ethanol
Continuous Vents	None							
Intermittent Vents	Distillation, reaction loop, relief valves					Y		
Water Systems						Y		
Fugitive Emissions	Valves/Flanges					Y		Ethanol
Typical Release Quantity	***% of Total Throughput***					-		-
ETHYL BENZENE								
Tanks & Loading	Storage Tank Vents					Y		
Continuous Vents	Flare	Y	Y	Y	Y	Y	Y	
	De-ethaniser					Y		
Intermittent Vents	Safety Valves, Catalyst Regeneration	Y	Y	Y	Y	Y	Y	
Fugitive Emissions	Flanges, Seals	Y	Y	Y	Y	Y		
Typical Release Quantity	***% of Total Throughput***	-	-	-	-		-	-
ETHYLENE								
Tanks & Loading						Y		
Intermittent Vents	Safety Valves					Y		
Process Design	Furnace/Cooker Stacks, Decokers, Regen. Heater	Y	Y	Y	Y	Y		
Fugitive Emissions	Valves/Flanges					Y		
Typical Release Quantity	***% of Total Throughput***	*3*	*0.01*	*0.01*	*0.1*	*0.7*		

[1] Particulates

Table 3.7 Petrochemical processes: types of release to air (Cont.)

	Release Source	CO_2	CO	SOx	NOx	VOC	Part[1]	Other
ETHYLENE OXIDE/ETHYLENE GLYCOL								
Continuous Vents	Process Purges	Y				Y		
	Stripper Vents	Y				Y		
	Vacuum systems	Y				Y		
Intermittent Vents	Tanks	Y				Y		Ethyl Chloride
	Gas Purge							
Typical Release Quantity	***% of Total Throughput***	***63***				***0.20***		***trace***
HIGHER OLEFINS								
Tanks & Loading	Storage Tank Breathers		Y			Y		
Continuous Vents	Flare	Y	Y		Y	Y		
	Compressor Vents					Y		Ethylene
Intermittent Vents	Emergency S/D							
Process Design	Catalyst Regeneration	Y	Y			Y		
Water Systems	Drips Collection System					Y		Solvent
Fugitive Emissions	Valves/Flanges					Y		
Typical Release Quantity	***% of Total Throughput***	***0.2***	***0.3***	***Trace***	***Trace***	***0.1***		***0.2***
ISOPROPYL ALCOHOL								
Tanks & Loading	Storage Tank Breathers					Y		
Continous Vents	None							
Process Design	Reaction loop, distillation					Y		Methane, Ethane, Propane
Fugitive Emissions	Valves/Flanges					Y		Methane, Ethane, Propane
Typical Release Quantity		-				-		-
VINYL ACETATE MONOMER								
Tanks & Loading	Storage Tank Breathers					Y		
Intermittent Vents	Relief valves					Y		
Process Design	Reaction Loop, Distillation Train	Y				Y		Ethylene, Inert Gases
	CO_2 Removal Plant	Y						
Fugitive Emissions	Valves/Flanges					Y		
Typical Release Quantity	***% of Total Throughput***	***0.09***				-		***0.016***

[1] Particulates

Table 3.8 Petrochemical processes: types of release to water

	Release Source	BOD	SS	DS	HC	P	N	Orgs	Hg	Metals
CUMENE										
Process Spillages/Washwater	Gravity Separation				Y	Phosphoric Acid				
Typical Release Quantity	*%*				-	-				
ETHANOL										
Process Spillages/Washwater					Y			Y		
	%				-					
ETHYL BENZENE										
Process Spillages/Washwater	Sour Water	Y	Y	Y	Y					
Typical Release Quantity	*%*	-	-	-	-					
ETHYLENE										
Process Spillages/Washwater	Sour Water Stripper, Caustic Wash, Cooker Discharges	Y			Oil		NH3	Y		Zn/Cr, Zn/P, Cu
Typical Release Quantity	*%*	-			*0.06*			*0.2*		-
ETHYLENE OXIDE/ETHYLENE GLYCOL										
Process Purges		Y			Y					
Typical Release Quantity	*%*	*0.3*			*0.3*					
HIGHER OLEFINS										
Process Spillages/Washwater	Olefin Wash	Y					Y		Ni	Aldehydes, Formate, Ion
	Aqueous Effluent	Y	Y		Phosphates		Y			
Typical Release Quantity	*%*	*0.3*			-		*0.4*		*Trace*	-
ISOPROPYL ALCOHOL										
Process Spillages/Washwater		Y						Y		
Typical Release Quantity	*%*									
VINYL ACETATE MONOMER										
Process Effluent	Equipment wash	Y						Y		
Typical Release Quantity	*%*									

Table 3.9 Petrochemical processes: types of release to land

			Inert	Liq Org	Aqueous	Special Wastes	Other
CUMENE	Spent Catalyst, Catalyst support, Sludges from acid			Y		Y	
Typical Release Quantity		*%*		*0.02*		*0.06*	
ETHANOL							
Typical Release Quantity							
ETHYL BENZENE	Spent Catalyst, Spent Molecular Sieve Material, Alumina					Y	
Typical Release Quantity		*%*					
ETHYLENE	Coke, DEA, Tar, Spent Catalyst			Y			
	Asbestos, ash					Y	
Typical Release Quantity		*%*			*0.2*	*0.6*	
ETHYLENE OXIDE/ ETHYLENE GLYCOL	General factory waste and cooling water sludge						Y
Typical Release Quantity		*%*					*na*
HIGHER OLEFINS	Vessel Residues, Organic Slops, Catalyst sludge,		Ash	Y	Y	Y	
	Fixed bed catalyst					Y	
Typical Release Quantity		*%*		*0.2*		*0.03*	
ISOPROPYL ALCOHOL							
Typical Release Quantity		*%*					
VINYL ACETATE MONOMER							
Typical Release Quantity		*%*					

Table 3.10 Acid and Aldehyde processes: types of release to air

	Release Source	CO_2	CO	SOx	NOx	VOC	Part[1]	Other
ACETIC ACID								
Tanks & Loading						Y		Methyl Iodine
Continuous Vents	Process Offgas flare	Y	Y					Methanol
	Process Boilers	Y	Y	Y	Y			Acetic anhydride
	CO Production	Y	Y	Y	Y	Y		Iodine
Intermittent Vents						Y		Acetic Acid
Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*	*na*	*na*	*na*	*na*	*na*		
ACETYLENE								
	Storage Tanks					Y		Acetone
	Plant Purifier & Manifold Venting, Feed Hopper Venting			Y		Y		Ammonia, Acetylene, H_2S, Phosphine, Nitrogen
	Cylinder Venting, Emergency Relief Vents			Y		Y		Ammonia, Acetylene, H_2S, Phosphine, Acetone
	Valves/Flanges					Y		
Typical Release Quantity	*% of Total Throughput*			*na*		*na*		*na*
ADIPIC ACID								
Tanks and Storage						Y		
Continuous Vents	Reactor Offgas	Y	Y	Y	Y	Y		Boron, Cr,NH_3,N_2O
Intermittent Vents	Relief/Blowdown					Y		Boron, Cr,NH_3,N_2O
Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*	*na*	*na*	*na*	*na*	*na*		
DIMETHYL ETHER (DME)								
Tanks & Loading	Storage Tank Vents						Y	Methanol
Intermittent Vents	Safety Valves, Inerts Vent						Y	Methanol, Nitrogen, DME
Continuous Vents	Flare, Dimethylether Unit	Y	Y		Y			Methanol, DME
Fugitive Emissions							Y	
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*		*na*	*na*
FORMALDEHYDE								
Tanks & Loading	Storage Tank Vents					Y		Formaldehyde, Methanol
Continuous Vents	Tail Gas Incinerator	Y	Y		Y	Y		
Fugitive Emissions	Flanges, Seals					Y		Formaldehyde, Methyl Formate, Formic Acid
Typical Release Quantity	*% of Total Throughput*	*15.2*	*na*		*0.02*	*0.18*		*na*
PHTHALIC ANHYDRIDE								
Tanks & Loading	Storage Tank Vents					Y		
Continuous Vents	Condenser Off-gas, Boiler, Heaters, Flaking Machine, Still Scrubber & Vacuum System, Dust Melter	Y	Y	Y	Y	Y	Y	
Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*	*na*	*na*	*na*	*na*	*na*	*na*	
TEREPHTHALIC ACID								
Tanks & Loading	Storage Tank Vents					Y		Methane, Methyl Bromide, Hydrogen, Methanol, Methyl Acetate, Acetic Acid, Benzene, Paraxylene, Toluene
Continuous Vents	Atmospheric Absorber, Offgas, Flue Gas	Y	Y		Y			
Intermittent Vents	Safety Relief Valves					Y		
Fugitive Emissions								
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*	*na*		*na*
METHACRYLIC ACID								
Continuous Vents	***Vent gas burner***	Y	Y	Y	Y			
	Reactor vents			Y		Y		
	Distillation vents					Y		
Tanks & Loading						Y		
Typical Release Quantity	*% of Total Throughput*	*na*	*na*	*na*	*na*	*na*		

(1) Particulates

Table 3.11 Acid and aldehyde processes: types of release to water

	Release Source	BOD	SS	DS	HC	P	N	Orgs	Hg	Metals	Other
ACETIC ACID											
Process purges		Y							Y	Cd, Ni,Cu,Zn	
Typical Release Quantity	*%*	*na*							*na*	*na*	
ACETYLENE											
Process Spillages/Washwater	Site Sewage System		Y		Oil		Y				Ca Hydroxide
Typical Release Quantity	*%*	*Min*			*0.03*		*0*				*na*
DIMETHYL ETHER (DME)	*To WWTP*										
Process Spillages/Washwater	Methanol Stripper	Y		Y	Y			Y			ACN, Methanol
Typical Release Quantity	*%*	*na*		*na*	*na*			*na*			*na*
ADIPIC ACID											
Process purges		Y		Y				Y		Cu	NH_3
Typical Release Quantity	*%*	*na*		*na*				*na*		*na*	*na*
FORMALDEHYDE											
Process Spillages/Washwater	Cooling Water, Gland Water to WWTP	Y	Y					Y			
Typical Release Quantity	*%*	*na*	*na*		*na*						
PHTHALIC ANHYDRIDE											
Process Spillages/Washwater	Runoff to Estuary	Y	Y					Y	Y	Cu, Zn, Pb, Fe	
Typical Release Quantity	*%*	*na*	*na*		*na*				*na*	*na*	
TEREPHTHALIC ACID											
Process Spillages/Washwater	Waste Drain, Manhole	Y	Y			Zn Phosphate		Y	Y	Cadmium	na Hydroxide
Typical Release Quantity	*%*	*na*	*na*			*na*		*na*	*na*	*na*	*na*
METHACRYLIC ACID											
Continuous	Cooling Water Purge									Zn	
	Waste Water to ETP	Y									
Typical Release Quantity	*%*	*na*								*na*	

Table 3.12 Acid and aldehyde processes: types of release to land

	Release Source		Inert	Liq Org	Aqueous	Special Wastes	Other
ACETIC ACID *unable to determine from authorisation*							
ACETYLENE	Generator waste				Carbon, lime, alkaline earth metals, Hg, Arsenic,		
Typical Release Quantity		%	*na*	*na*	*na*	*na*	
DIMETHYL ETHER (DME)	Alumina-Silica Catalyst, General		Y			Y	
Typical Release Quantity		%	*na*			*0.003*	
ADIPIC ACID *Process*	Organic purge					Y	Boron
Typical Release Quantity		%					
FORMALDEHYDE	Spent Catalysts						
Typical Release Quantity		%	*na*			*na*	
METHACRYLIC ACID	Polymer byproducts for cleaning equipment					Y	
Typical Release Quantity		%	na				
PHTHALIC ANHYDRIDE	Alkali/Organic Sludges			Y			
	Organic Polymers, tank sludge					Y	
Typical Release Quantity		%	*na*	*na*		*3.5*	
TEREPHTHALIC ACID	Alumina desiccant, Cooling Tower Waste, Catalyst, Contaminated Factory Waste, Residue Solids					Y	
Typical Release Quantity		%	*na*	*na*		*0.30%*	

Table 3.13 Sulphur processes: types of release to air

	Release Source	CO_2	CO	SOx	NOx	VOC	Part[1]	Other
SULPHENAMIDES								
Tanks & Loading	Storage Tank Breathers					Y		H2S, Aniline, MBT
	Storage bunds					Y		Carbon disulphide
Continuous Vents	Burner Vents, Airblowing Vent, MBT Strong Effluent Sump, Dust Collector Exhausts, Filter Extraction Hood Exhaust	Y	Y		Y	Y	Y	Aniline, MBT, Carbon Disulphide
Intermittent Vents	Bursting discs					Y	Y	
Process Design	Stripper Condenser Vent, SRU Tank Vent, Toluene Recovery Vent			Y		Y	Y	
Fugitive Emissions	Valves/Flanges					Y		
Typical Release Quantity	***% of Total Throughput***	***na***	***na***	***na***	***na***	***na***		***0.12***
SULPHATE SURFACTANTS								
Tanks & Loading	Storage Tank Breathers					Y		Acid, Caustic
Process Design	Reactor vents					Y		HCl
Fugitive Emissions	Valves/Flanges							
Typical Release Quantity	***% of Total Throughput***					***Trace***		***na***

(1) Particulates

Table 3.14 Sulphur processes: types of release to water

	Release Source	BOD	SS	DS	HC	P	N	Orgs	Hg	Metals	Other
SULPHENAMIDES											
Process Spillages/Washwater	Treated effluent, Emergency Discharge, Stormwater	Y	Y					Y			Phenol, cresol, sulphen-amides
Typical Release Quantity	*%*	*na*	*na*		*na*						*na*
SULPHATE SURFACTANTS											
Loading/Storage	Drum washwater	Y						Y			
Process Spillages/Washwater	Redundant Raw materials	Y						Y	Y		Acid, Amine
	Acidic liquors			Y							
	Non-special waste	Y						Y			
Typical Release Quantity	*%*	*17*			*na*						*na*

Table 3.15 Sulphur processes: types of release to land

			Inert	Liq Org	Aqueous	Special Wastes	Other
SULPHENAMIDES	Spent catalysts						Y
	Cobalt metal scale						Y
	Spent solution						Y
Typical Release Quantity		%					Recycled
SULPHATE SURFACTANTS	Redundant Raw Materials, Special Waste, Non-special Waste						Y
	Special waste					Y	
	Non-special waste		Y				
Typical Release Quantity		%	*16*			*4*	*1*

Table 3.16 Nitrogen processes: types of release to air

NITROBENZENE	**Release Source**	**CO_2**	**CO**	**SOx**	**NOx**	**Metals**	**VOC**	**"Part"**	**Other**
Tanks & Loading	Storage Tanks, Aliphatic Tanker Loading						Y		Benzene, SO_3
Continuous Vents	Effluent Treatment Tanks, NOx Scrubber Vent (to Thermox)	Y	Y		Y			Y	Benzene, nitrobenzene, ammonia
	Thermal Oxidiser Tail Gas Stack	Y	Y	Y	Y				NO/N2O
Intermittent Vents	Emergency Relief Vents						Y	Y	Benzene, Nitrobenzene
Fugitive Emissions	Valves/Flanges						Y		Benzene, Nitrobenzene
Typical Release Quantity	*% of Total Throughput*	*15*	*0.008*	*0.003*	*0.05*		*0.01*	*Trace*	

ANILINE	**Release Source**	**CO_2**	**CO**	**SOx**	**NOx**	**Metals**	**VOC**	**Dust**	**Other**
Tanks & Loading	Storage Tank Breathers						Y		Benzene, Aniline, Nitrobenzene
Continuous Vents	Aniline Reactor Vent, Furnace, Hydrogen System Vent, Molecular Sieves	Y	Y		Y	Y	Y		Benzene, Aniline, Methane, Hydrogen
Intermittent Vents	Non-Reactor Vents, Emergency Relief Valves, Analysers						Y		Benzene, Aniline, Ammonia, Hydrogen
Process Design	Nitrobenzene Extractor						Y		Nitrobenzene
Fugitive Emissions	Valves/Flanges						Y		
Typical Release Quantity	*% of Total Throughput*	*1.9*	*0.002*		*0.006*	*Trace*	*na*	*0.001*	*0.4*

METHYLAMINES									
Tanks & Loading	Storage Tanks, Effluent Collection Tanks, Road/Rail Filling Absorber					Hg	Y		Methanol
Process Design	Off-Plots Absorber				Y	Hg	Y		
Continuous Vents	Flare Stack	Y	Y		Y	Hg			
Intermittent Vents	Pressure Relief						Y		
Fugitive Emissions	Valves/Flanges						Y		
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*	*na*	*na*		*na*

Table 3.16 Nitrogen processes: types of release to air (Cont.)

	Release Source	CO_2	CO	SOx	NOx	Metals	VOC	Dust	Other
NITROBENZENE									
Tanks & Loading	Storage Tanks, Effluent Collection Tanks						Y		Higher Amines, Alcohols, Ammonia
Continuous Vents	Flare Stack	Y	Y		Y				
Intermittent Vents	Pressure Relief						Y		Higher Amines, Alcohols, Ammonia
Fugitive Emissions	Valves/Flanges						Y		
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*		*na*		
AMINE BASED SURFACE ACTIVE CHEMICALS									
Intermittent Vents	Scrubber vent						Y		
	Dryer/Grinder							Y	
	Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*						*2*	*na*	
ACRYLONITRILE									
Continuous Vents	Absorber vents	Y	Y		Y		Y		HCN, NH3
Intermittent Vents	Tank breathing						Y		
	Flare System	Y	Y						
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*		*na*		
ADIPONITRILE									
Continuous Vents	Synthesis Offgas						*Y*		Hydrogen, ACN
	Absorber vents	Y	Y		Y		Y		
	Vacuum exhausts						Y		
Intermittent Vents	Tank breathing						Y		
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*		*na*		
HEXAMETHYLENE DIAMINE									
Continuous Vents	Vacuum exhausts						Y		
Intermittent Vents	Tank breathing						Y		
	Flare System	Y	Y						
Typical Release Quantity	*% of Total Throughput*	*na*	*na*				*na*		
DIMETHYL FORMALDEHYDE/DIMETHYLACETAMIDE/CHOLINE CHLORIDE /DIMETHYL AMINOETHANOL									
Intermittent Vents	Scrubber						Y		
	Flare	Y	Y		Y				
Tanks/loading	Breathing						Y		
	Vent scrubber						Y		HCl
Typical Release Quantity	*% of Total Throughput*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*na*

Table 3.17 Nitrogen processes: types of release to water

	Release source	BOD	SS	DS	HC	P	N	Orgs	Hg	Metals	Other
NITROBENZENE											
Weak effluent stream		Y					Ammoniacal plus nitrates, nitrites etc.	Y	Y	Cadmium	
Strong effluent stream		Y	Y	na oxalate and inorganic salts				Y			Nitrobenzene, Nitrophenols
Typical Release Quantity	*%*	*0.02*	*na*	*0.541*	*Trace*		*Trace*		*na*	*na*	
ANILINE :											
Process Spillages/ Washwater	NB Extractor, Reactor Residues, Wet Purge, Batch Still Waste, Furnace	Y		Y	Benzene, Aniline, Nitrobenzene, Cyclohexylamine,		Ammonia, Organic Amide			Ni Catalyst	Inorganic Lime, na Hypochlorite, Hydrazine Soln
Typical Release Quantity	*%*	*Min*		*na*	*0.03*		*0.05*			*na*	*na*
METHYLAMINES											
Process Spillages/ Washwater	Process Effluent to Sewers	Y	Y	Y	Methyl- amines, Higher amines					Hg	
Typical Release Quantity	*%*	*na*	*na*	*na*	*na*					*na*	
ETHYLAMINES											
Process Spillages/ Washwater	Discharge from scrubbing systems, Blow downs	Y	Y	Y							Higher amines, Alcohols
Typical Release Quantity	*%*	*na*	*na*	*na*							*na*
ACRYLONITRILE											
Process Effluent	Reaction product	Y	Y			HCN				Y	Ammoniacal Nitrogen
Typical Release Quantity	*%*										
ADIPONITRILE											
Process Effluent	Reaction product	Y	Y							Y	
Typical Release Quantity	*%*										
AMINE BASED SURFACE ACTIVE CHEMICALS											
Neutralised effluent	Process Spillages/ Washings	Y	Y	Y	Y				Y	Cd	
Typical Release Quantity	*%*	*na*	*na*	*na*	*na*				*na*	*na*	
DIMETHYL FORMALDEHYDE/DIMETHYLACETAMIDE/CHOLINE CHLORIDE/DIMETHYL AMINOETHANOL											
Reed bed feed	Scrubber liquor Vessel Washings Blowdown	Y			Amides			Y			
Typical Release Quantity	*%*	*na*			*na*			*na*			
HEXAMETHYLENE DIAMINE											
	Process purges	Y									Ammonia
Typical Release Quantity	*%*	*na*									

Table 3.18 Nitrogen processes: types of release to land

			Inert	**Liq Org**	**Aqueous**	**Special Wastes**	**Other**
NITROBENZENE	Process Effluent, General Waste		Y	Y			
Typical Release Quantity		*%*	*na*	*na*			
ANILINE	Batch Still, Spent Catalyst Filters, General Waste, Catalyst Drums, Water Treatment Chemical Drums		Y	Aniline	Phenol		Anil, Tars, Ni Catalyst
Typical Release Quantity		*%*	*15*	*1200*	*na*		*na*
METHYLAMINES							
	General, process wastes				Y	Y	
Typical Release Quantity		*%*	*na*			*na*	
ETHYLAMINES							
						Y	With Ni
Typical Release Quantity		*%*	*na*	*na*		*na*	
ACRYLONITRILE							
	Ammonium Sulphate cake sludge		Y			Y	
	Residues			Y		Y	Metal Oxides and nitrile polymers
Typical Release Quantity		*%*	*na*	*na*		*na*	
ADIPONITRILE							
	Scrap electrodes		Y			Y	1% Cd
	Cadmium sump sludge		Y	Y		Y	Cd, organic tars
Typical Release Quantity		*%*	*na*	*na*		*na*	
AMINE BASED SURFACE ACTIVE CHEMICALS							
Special Process Wastes						Y	
HEXAMETHYLENE DIAMINE							
	Spent Catalyst					Y	
Typical Release Quantity		*%*				*na*	

Table 3.19 Monomer and polymer processes: types of release to air

	Release Source	CO_2	CO	SOx	NOx	VOC	"Part"	Other
EDC/VCM								
Tanks & Loading	Storage Tank Breathers					Y		HCl, EDC
Continuous Vents	Cracker/Flue Stack,	Y	Y		Y	Y		HCl, EDC, VCM, Ethylene
	Vents Product Phase Separator, Direct Chlorinators, Oxychlorinators					Y		HCl, EDC, VCM, Ethylene
Intermittent Vents	Emergency/Thermal Relief Valves					Y		HCl, EDC, VCM, Ethylene
Fugitive Emissions	Valves/Flanges					Y		HCl
Permitted Release Quantity	***% of Total Throughput***	***na***	***na***		***na***	***0.4***		***(VCM 0.6kg/ton)***
PVC								
Tanks & Loading	Storage Tank Breathers, Slurry Stock Tank Vents					Y		VCM, PVC
Continuous Vents	VCM Recovery Plant Vents					Y		VCM
	Flash & fluid bed drier vents					Y	Y	VCM, PVC
	Conveying System					Y	Y	VCM, PVC
Intermittent Vents	Process Upsets, Reactor/ Stripper Evacuation					Y		VCM
Fugitive Emissions	Valves, Flanges					Y		VCM
Permitted Release Quantity	***% of Total Throughput***					***na***	***na***	***(VCM 0.25 kg/ton)***
STYRENE								
Tanks & Loading	Storage Tanks					Y		Ethyl- benzene, Styrene, Catalyst, Inhibitors, Filming
Continuous Vents	Vent to fuel	Y	Y		Y	Y		
	Distillation inerts					Y		
Intermittent Vents	Pressure relief to flare	Y	Y		Y	Y		
Fugitive Emissions	Valves/Flanges					Y		
Typical Release Quantity	***% of Total Throughput***					***0.01***		***Trace***
STYRENE RUBBER (SBR)								
Tanks & Loading	Storage Tanks					Y		
Process Design	Monomer Recovery Vents					Y		H_2S, CS_2, Butadiene
Continuous Vents	Flare, Drier Vents, Vacuum Pump Vents	Y	Y		Y	Y		
Intermittent Vents	Pressure Relief Valves					Y		
Fugitive Emissions	Valves/Flanges					Y		
Typical Release Quantity	***% of Total Throughput***					***0.1***		***Trace***

Table 3.19 Monomer and polymer processes: types of release to air (Cont.)

	Release Source	CO_2	CO	SOx	NOx	VOC	Dust	Other
POLYSTYRENE								
Tanks & Loading	Drips Collection vessel, Storage Tank Vents					Y		Ethyl- benzene, Styrene, Toluene
Continuous Vents	Flare, Compressor vents, Hotwell vents, Incinerator	Y	Y		Y			
Intermittent Vents	Catalyst preparation vents, Catalyst regeneration vents							
Fugitive Emissions	Valves/Flanges							
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*	*na*		*Trace*
METHYL METHACRYLATE								
Tanks & Loading	Storage Tank Vents					Y		Methane, Methanol, Ammonia, Acetone, MMA, HCN
Continuous Vents	Amide Mixers & Reactors, Primary Cooler, other vents					Y		
	Tail Gas Burners	Y	Y	Y	Y	Y		Y
	Sulphuric acid recovery stack	Y	Y	Y	Y			
	Vacuum pumps			Y				HCN
Vents: Ammonium Sulphate	Vacuum system, Dryer vent						Y	Ammonium sulphate
Intermittent Vents	Flare stack					Y		
Fugitive Emissions	Flanges, Seals etc.					Y		
Typical Release Quantity	*% of Total Throughput*		*0.05*		*0.03*	*na*		*1.2*
ACRYLIC SHEET								
Tanks & Loading	MMA/DMMA, Resin Storage Tank Vents					Y		MMA
Intermittent Vents	Safety Valves					Y		MMA
Continuous Vents	Cooling Tower Vents, local Exhaust Ventilation					Y		
Process Design	Resin Reactor Vents, Batch Vessel Vents, Polymerisation Oven Vents					Y		MMA, PVC
Fugitive Emissions						Y		MMA
Typical Release Quantity	*% of Total Throughput*	*na*	*na*		*na*	*na*		*na*
POLYACRYLAMIDE								
Tanks & Loading	Storage Tank Vents						Y	
Intermittent Vents	Safety Relief Valves							
Process Design	ACM Process/Catalyst Scrubber Exhaust						Y	
Fugitive Emissions							Y	
Typical Release Quantity	*% of Total Throughput*						*na*	

Table 3.19 Monomer and polymer processes: types of release to air (Cont.)

	Release Source	CO_2	CO	SOx	NOx	VOC	Dust	Other
NITRILE RUBBER								
Tanks & Loading	Storage Tank Vents					Y		Acrylo- nitrile, Butadiene, Mercaptans
Continuous Vents	Tank Reactor Vents					Y		Acrylo- nitrile
	BD Monomer Recovery					Y		Butadiene
Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*					*na*		*0.2*
LPDE								
Intermittent vents	Relief valves to flare	Y	Y		Y	Y		
	Compressor seal leaks					Y		
	Decompressions					Y		
Process Design	Purge gas, Degasser air					Y	Carbon	
Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*					*1.9*		
POLYPROPYLENE								
Intermittent Vents	Shutdown Vent to Flare	Y	Y		Y	Y		
Process Design	Propane bleed to flare	Y	Y		Y	Y		
	Solids Handling						Y	
Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*	*13*	*0.02*		*0.06*	*2.1*		
POLYESTERS								
Tanks & Loading	Storage Tank Vents					Y		Mono/ Diethylene glycol, Butane 1,4 diol, Polyester
Process Design	Polyester Reactor Vents, Exhaust Ventilation					Y		Dihydric Alcohols
Fugitive Emissions						Y		
Typical Release Quantity	*% of Total Throughput*					*Trace*		*Trace*
POLYESTER RESINS								
Tanks & Loading	Storage Tank Vents, Drumming-off Area					Y		Styrene
Intermittent Vents	Safety Valves, Local Exhaust Ventilation (LEV's)					Y		Styrene, N_2
Process Design	Reactor Vents					Y		Styrene, N_2
Fugitive Emissions						Y		Styrene
Typical Release Quantity	*% of Total Throughput*							
BUTYL POLYMERS (HALOGENATED)								
Tanks & Loading	Storage Tank Vents					Y		
Intermittent Vents	Safety Valves					Y		
Process Design	Scrubber vents					Y		Cl_2, Br_2
	Drier vent					Y		
Fugitive Emissions								
Typical Release Quantity	*% of Total Throughput*					*na*		

Table 3.20 Monomer and polymer processes: types of release to water

	Release Source	BOD	SS	DS	HC	P	N	Orgs	Hg	Metals	Other
EDC/VCM											
Process Spillages/ Washwater	Spent Catalyst, Per-Tri Drainings, Process Drainage, Residues	Y	Y					Chlorinated HC's, EDC	Y	Iron, Cu	Chloroform, Free Cl_2, CCl_4
Typical Release Quantity	*%*	*na*	*na*	*na*				*na*	*na*	*na*	*na*
PVC											
	Process effluent	Y	Y					Y	Y	Y	Free Cl2, EDC, VCM, CCl4, Chlorinated HC's, Cr,Pb,Cu,Zn
Typical Release Quantity	*%*	*na*	*na*	*na*	*na*			*na*	*na*	*na*	*na*
STYRENE											
Process Spillages/Washwater	HC Interceptor	Y	Y				Y	Y			
Typical Release Quantity	*%*	*na*	*na*		*na*		*na*	*na*			
STYRENE RUBBER (SBR)											
Process Spillages/Washwater	HC Interceptor	Y	Y				Y	Y			
Typical Release Quantity	*%*	*na*	*na*				*na*	*na*			
POLYSTYRENE											
Loading/Storage	Tank Cleanings	Y	Y		Y			Y			Ethyl- benzene Styrene, Rubber Soln
Process Spillages/Washwater	Process Discharge to trade-effluent system	Y	Y	Y	Y			Y			Ethyl- benzene Styrene, Rubber Soln
Typical Release Quantity	*%*	*0.001*	*na*	*na*	*na*			*na*			*0.003*
METHYL METHACRYLATE											
Process Spillages/Washwater	Process Effluent/ Stormwaters, Cooling water blowdown, Distillation Lights	Y	Y	Y			Ammo- niacal	Acetone	Y	Zinc	HCN
Typical Release Quantity	*%*	*0.03*	*0.003*	*na*				*na*	*na*	*na*	*0.01*

Table 3.20 Monomer and polymer processes: types of release to water (Cont.)

	Release Source	BOD	SS	DS	HC	P	N	Orgs	Hg	Metals	Other
ACRYLIC SHEET											
Process Spillages/Washwater	Process Effluent, Visible Oil, Grease, Polymer Gel	Y	Y	Y	Y				Y		
Typical Release Quantity	*%*	*na*	*na*	*na*	*na*				*na*		
POLYACRYLAMIDE											
Process Spillages/Washwater	ACM Process Drainage, Process Vessel Wash-out	Y					Ammonia		Y	Cu, Cadmium	Acrylamide
Typical Release Quantity	*%*	*0.4*					*0.01*		*Trace*	*0.01*	*0.2*
NITRILE RUBBERS											
Process Spillages/Washwater	Coagulation etc	Y	Y								ACN, Methanol
Typical Release Quantity	*%*	*na*	*na*								*0.4*
LDPE											
Process Spillages/Washwater	Process Effluent/Outfall	Y			Y				Y		
Typical Release Quantity	*%*	*na*	*na*	*na*	*na*				*Trace*		
POLYPROPYLENE											
Process Spillages/Washwater	Process Effluent/Overflow	Y	Y		Y				Y		
Typical Release Quantity	*%*	*Small*	*Small*	*Small*	*Small*				*na*		
POLYESTERS											
Process Spillages/Washwater	Process Effluent, Polyester Liquid Effluent	Y	Y					Y			
Typical Release Quantity	*%*	*na*	*na*	*na*				*na*			
POLYESTER RESINS											
Process Spillages/Washwater	Glycol Contaminated Water,	Y	Y	Y				Y			Xylene, Glycol
Typical Release Quantity	*%*	*na*	*na*	*na*				*na*			
BUTYL POLYMERS (HALOGENATED)											
Process Spillages/Washwater	Process Effluent	Y		Y				Y			Ca stearate
Typical Release Quantity	*%*	*na*	*na*	*na*	*na*				*na*		

Table 3.21 Monomer and polymer processes: types of release to land

			Inert	Liq Org	Aqueous	Special Waste	Other
EDC/VCM	VCM Purification, Vessel Emptying, Process Waste		Y	Y		Spent Lime	
Typical Release Quantity		*%*	***na***	***na***		***na***	
PVC	Effluent tank waste					Y	
	Sludges		Y				
Typical Release Quantity		*%*	***na***	***na***			
STYRENE	Spent Catalyst					Y	
	Waste Residue, Filter Cake, Styrene Polymer			Y		Y	
	General		Y				
Typical Release Quantity		*%*	***na***	***na***		***na***	
STYRENE RUBBER (SBR	Polymer wastes		Y				
Typical Release Quantity		*%*	***na***			***na***	
POLYSTYRENE	Reactor Solids, Rubber Crumbs, Lubricating Agent		Y	Y		Y	
Typical Release Quantity		*%*	***0.6***	***Trace***		***0.07***	
METHYL METHACRYLATE (MMA)	Waste polymers/tars			Y			
	Furnace ash					Y	
	Spent catalyst, desiccant, equipment internals					Y	
Typical Release Quantity		*%*		***na***		***na***	

Table 3.21 Monomer and polymer processes: types of release to land (Cont.)

			Inert	Liq Org	Aqueous	Special Waste	Other
ACRYLIC SHEET	Used Filters/Wipes and General waste		Y	Y			
Typical Release Quantity		%	*na*	*na*			
NITRILE RUBBERS	Drier Scrap		Y				
	Effluent sludge			Y			
Typical Release Quantity		%	*na*	*na*	*na*		
POLYACRYLAMIDE	Spent Catalyst, General		Y			Y	
Typical Release Quantity		%	*na*			*na*	
LDPE	Blowdown Oils			Y			
	Waxes		Y				
Typical Release Quantity		%	*0.02*				
POLYPROPYLENE	Filter Dust		Y				
	Organics to incineration			Y			
Typical Release Quantity		%	*0.04*	*0.01*			
POLYESTER	Spent Catalyst, Waste Solvents, General Waste		Y	Y		Y	
Typical Release Quantity		%	*na*	*na*		*na*	
POLYESTER RESINS	Unsaleable Stock		Y				
Typical Release Quantity		%	*na*				
BUTYL POLYMERS	Spent Catalysts					Y	
	Oily/Polymers Wastes			Y			
	WWTP Sludge			Y			
Typical Release Quantity		%	*na*	*na*		*na*	

3.3.2. Summary of types of release

The releases to the environment fall into a number of common groupings, plus some sources that are not typical of the processes reviewed. The common categories are summarised for releases to air, water and land in the following sections.

Releases to air

One of the most common types of emission, and particularly characteristic of this group of processes, is that of Volatile Organic Compounds (VOCs). From the data available, the quantity of VOC emitted ranges from 0.01 percent of total production to over two percent. The losses at the higher end of the scale are those associated with processes where the feedstock, or one of the main process streams, is a gas (or would be at ambient conditions). Polyolefin production is an example of this type of process. Several types of VOC release are hard to measure, however, and estimates of emissions can be very inaccurate, so these figures should be taken only as indicative.

Reported sources of VOC emissions include the following.

- Losses occur from tank vents and on loading or unloading of mobile containers (road or rail tankers). The stored or transferred material may be an organic feedstock, process stream or product, or a solution or slurry (such as PVC reactor slurry). Effluent tanks or basins are also possible sources of emissions.

- Intermittent releases of VOCs occur from several sources. Those reported include safety relief systems, start-up and shut-down procedures, and purging of reactors or other equipment prior to periodic descaling or maintenance. Inerts bleeds, from condensers, for example, may be periodic if the system is substantially inert-free.

- Fugitive emissions may arise from leaks in flanges, around valve stems, or from the seals of compressors or pumps.

- Losses of VOCs from water systems are reported only occasionally, mainly from drains and from drip collection systems.

- The most diverse, and process-specific, category of VOC release is that of substantially continuous vent streams. The sources include vents from process scrubbers, continuous inert vents from condenser, purge gas from recycle loops, vents from polymerisation ovens or drying ovens, reactor vents, compressor vents, and exhausts from ventilation systems.

The other main category of emission is that arising from combustion associated directly with the process. Some of the VOC emissions identified above will in practice be fed to a combustion device before discharge. In addition to any unburnt organics, the emissions will include carbon dioxide, carbon monoxide, and oxides of nitrogen. Other combustion products depend on the composition of the stream, and might include SO_2 and other acid gases. Combustion sources are identified as:

- process furnaces and fired process heaters
- incinerators operating on combustible streams, usually gaseous streams containing VOCs
- catalyst regeneration units, where the catalyst is typically decoked by burn-off
- site flare system, taking intermittent or emergency flows but also sometimes a continuous purge
- Off-gases from oxidation processes such as terephthalic acid and ethylene oxide.

Data quoted on emissions from combustion devices are very patchy, but the quantities will be closely related to energy consumption, other than power, on the plant. As the energy is consumed as steam in many cases, and the emissions therefore arise from "combustion plant" rather than the process, it is difficult to generalise. A gross energy consumption of around 0.05 to 0.20 tons oil equivalent, including steam, per ton of product is fairly typical for the processes reviewed. The selection of process and, moreover, the attention to energy integration of process streams, has a major effect on material and energy efficiency.

Other sources of release are process-specific. They include, for example, emissions of nitrous oxide from adipic acid production, or the emissions of reagents and by-products such as hydrogen sulphide.

Releases to water

In many cases, any liquid effluents pass to a site wastewater treatment facility. Effluents from individual processes do not appear to be quoted independently on all authorisations and the original source is often not transparent. The main types of source of wastewater are identified as follows.

- Spills and leaks arise from process plant and around storage tanks or loading facilities, which are washed intentionally or by rainwater into the site drainage system, usually passing through a hydrocarbon interceptor of some sort.

- Purges are exported from cooling water systems, pump gland water, and boiler blowdowns, although some of these may also be part of site rather than process facilities.

- Washwater arises not only from external cleaning of plant, but from periodic cleaning out of tanks or process equipment.

- An aqueous phase might be an intrinsic part of a process, either because water is in the feedstocks or produced in the reactions, or because the aqueous phase is necessary for the processing. Examples include the aqueous phase in a PVC or polypropylene slurry, liquors from some rubber coagulation systems, and stripper bottoms from production of oxygenated organics.

- Water or aqueous solutions are also used in unit operations such as vent gas scrubbers or direct contact condensers. Examples include desalter effluent, caustic wash from steam crackers, and effluent from amine scrubbers.

Releases to land

Releases to land fall into several main categories, as noted below.

- Many of the arisings are of spent beds used for processing purposes. Examples include catalysts, molecular sieves, other dessicants and purifiers.

- Residues or by-products from processing operations include tars or waxes from distillation, chlorinated by-products from EDC production, or by-product organic acids from adipic acid or terephthalic acid production.

- Spent reagents, often in sludge form, include amines for gas cleaning and spent solvents.

- Unused materials include raw materials or reagents, water treatment chemicals etc. Examples of off-specification solid product are rubber crumb and drier scrap.

- Sludges arising directly from the process might arise from on-plant neutralisation, waste water treatment, or as organic slop from processes with some presence of water.

3.3.3. Pollutants of interest

Some pollutants are of particular environmental interest because of toxicity or contribution to problems such as stratospheric ozone depletion, global warming or tropospheric ozone creation. Pollutants of interest arising from the petrochemical and large volume organic processes are summarised below. The pollutants are identified as far as possible from the authorisations reviewed and knowledge of the production processes.

Releases to air

Proposals have been made for ranking VOCs by environmental effect (Environment Agency report: The Categorisation of Volatile Organic Compounds, September 1995). This ranking is used in identifying pollutants of interest. Only VOCs categorised as of High or Medium impact are noted on Table 3.22. These correspond to the Environment Agency's Class A category. Selected non-VOCs are also noted.

Releases to water

Organic compounds, present either as an oil phase or dissolved in water, are an almost universal constituent of aqueous effluents from petrochemical and large scale organic processes. As noted above, process effluents are very often directed to a site wastewater treatment facility. In addition to the removal or destruction in such a facility, there is also a dilution effect resulting from the mixing of several effluent streams. The dilution effect may aid the wastewater treatment process by bringing concentrations of pollutants below the level at which they may be tolerated by biomass. For these reasons, individual pollutant species are not always identified in the IPC applications and authorisations. Conversely, the mixing of different chemical species may produce more harmful or untreatable effluents and this needs to be taken into consideration by Inspectors.

The aqueous pollutants of particular interest include those that may not be removed or destroyed by conventional water treatment or subsequently in the receiving water, or that are or particular environmental concern. Possible categories include the following.

- Organics that are difficult to degrade are generally more characteristic of fine chemical production than petrochemicals or large scale organics. Aqueous effluents from nitrobenzene production, however, falls into this category with derivatives of picric acid that colour the effluent yellow or red. Other compounds that are potentially difficult to degrade include long chain aliphatics and ring compounds such as phenolic compounds.

- Chlorinated organics are often of particular concern because of fears of bioaccumulation and long term effects. Once more, this category includes many pesticides rather than petrochemical or large scale organic wastes. However, aqueous effluents from the EDC to PVC chain potentially contain chlorinated hydrocarbons that require attention.

Table 3.22 Atmospheric pollutants of interest

Pollutant	Possible source processes	VOC category
Acetonitrile	Butadiene (ACN)	M
Acrylamide	Acrylamide	H
Acrylonitrile	Acrylonitrile and nitrile rubber	H
Aniline	Aniline	M
Benzene	Acetic acid, ethylbenzene/styrene, cumene, acetic anhydride, terephthalic acid, nitrobenzene, para-xylene	H
Buta-1,3-diene	Butadiene, rubber	H
Carbon disulphide	Carbon disulphide, viscose, SBR	H
Chlorinated hydrocarbons (C_1 & C_2)	EDC/VCM	M
Dioxins & furans	On-site combustion of chlorinated organics	
Dimethylformamide	Formaldehyde	M
Ethylene oxide	Ethylene oxide, ethylene glycol	H
Formaldehyde	Formaldehyde, resins	M
Hydrogen sulphide	Ethylbenzene, actylene etc	
Iodine	Acetic acid/acetic anhydride	
Mercury	Methylamine	
Methane	Aniline	M
Methylamine	Alkylamines	M
Methyl bromide	Terephthalic acid	M
Nickel	Higher Olefins , IPA (sludge incineration)	
Nitrobenzene	Nitrobenzene, aniline	H
Nitrous oxide	Adipic acid	
Olefins (ethylene, propylene, butylenes etc)	Ethylene (steam cracker), EDC, ethylbenzene, polyolefins (LDPE, LLDPE, HDPE, PP)	M
Styrene	Styrene, polystyrene	M
Vinyl chloride monomer (VCM)	EDC/VCM, PVC	H
Xylenes (e.g. mixed, para-xylene)	Terephthalic acid, para-xylene	M

- Concentrated waste streams, or those whose treatment is difficult because of the mixture of contaminants, may be treated more appropriately at the plant rather than in a common system. Caustic washes from petrochemical processes are a possible example.

- Metal-based pollutants, often deriving from catalyst residues, may be similarly significant. Examples include effluents with cadmium from terephthalic acid and nitrobenzene production, chromium from ethylene, nickel from aniline, and copper from EDC/VCM, adipic acid, and ethylene processes.

Releases to Land

Chemical species are often not identified for land wastes in existing IPC applications and authorisations. Producers are encouraged to minimise waste production under IPC, of course, but if wastes are produced, the producer has the duty of care for correct disposal. Identification of species is perhaps not necessary in this context.

Of the categories of releases to land identified above, perhaps the most relevant are those of residues/by-products and process sludges because on-site recovery or incineration might be relevant. Examples in this category include:

- chlorinated residues from EDC/VCM production
- waste organic streams from adipic acid production.

3.4 Abatement techniques used in the UK

3.4. 1 Review of IPC documents

An assessment was made of the abatement techniques typically in use in the UK by reviewing the selected IPC applications, authorisations and subsequent variations. Some reservations need to be noted. The results are illustrative rather than completely representative, and also originate only in England and Wales. The absence of a technique in an application might mean that it has not been reported rather than not adopted. In addition, although several of the authorisations have been revised since the first application, it must also be recognised that plants may have installed further measures that have not been recorded in the documents.

The techniques identified are presented on Tables 3.23 to 3.28. For convenience of presentation, the tables are split by category of process – petrochemicals, acids and aldehydes etc. – but several of the techniques apply across all categories.

3.4.2 Techniques to control emissions to air

The key techniques identified for control of VOC emissions to air are noted below.

Tanks and storage

- External floating roofs are common on storage tanks for more volatile liquids. A secondary seal is quoted on benzene and ethylbenzene storage on one plant.
- Internal floating roofs are also used, once more for more volatile liquids, with a criterion of C_9 olefins and below quoted in one case.
- Pressurised tanks, with pressure relief to flare or process, are used for maximum containment on, for example, amines.
- Balance lines are used on several plants, often via a header between operating tanks, or from tanks to process (VCM), or between tanks and mobile containers on loading/unloading.
- Tank level control techniques – to prevent overfilling – include operating procedures, level controls, high level alarm or, for critical duties, feed trip. One plant adopts a policy of normally filling to no more than 70 percent capacity.
- Cooling of tank feed is identified in one case (methyl methacrylate), and stability of tank temperature is recognised as an operating target in others.
- Losses from spills on loading are minimised by the common use of self-sealing flexible lines.

Table 3.23 Summary of control techniques: Petrochemical Processes

Control Technique		Cumene	Ethyl benzene	Ethylene	Alpha Olefins	Higher Olefins	Dimethyl Ether	EO and EG
Air Emissions								
NOx	Emission monitoring. Minimum practicable excess air levels to ensure clean combustion.	✓						
	Low NOx burners with staged-air or staged-fuel systems, coupled with good combustion control to minimise excess air to the burners.		✓	✓		✓		
CO_2	Ammonia injection system on HP boilers for reducing acidity in the flue gas & emission of acid soots		✓					
CO	Oxidation in CO boiler to carbon dioxide, liberating energy as steam.		✓					
VOCs								
Design	Recycle back to reactor. Small offtake to flare to prevent inert build up	✓						
	Solvent changed from toluene to p-tertiary butyl toluene, reducing vapour release quantities.				✓			
Sampling	Low-vapour loss sample points used for hydrocarbon streams		✓					
	Sampled via fast loop system		✓					
Design Standards	Flange minimisation, with high integrity flange joint materials.		✓					
	Drains and vents blanked and capped		✓					
	Low leak valves		✓					
Pumps	Dual mechanical seals and Ethyl Benzene seal fluid on pumps - benzene/ EB		✓					
	Pumps fitted with secondary lip seals plus mechanical seals		✓					
Thermal oxidiser				✓		✓		
Scrubbing system	N-anhydride						✓	
	Flash unit and scrubber to recover hydrocarbons from CO_2 purge							✓
Recovery to fuel	Packing leakage returned to process or to fuel gas system - ethylene compressor				✓			
	Process is designed such that HCs are recovered to the process or for use as fuel gas on the plant furnace				✓			
Leak Detection	Analysers are installed to detect ethylene leaks in the compressor houses so that these are dealt with promptly				✓			

Table 3.23 Summary of control techniques: Petrochemical Processes (Cont.)

Control Technique		Cumene	Ethyl benzene	Ethylene	Alpha Olefins	Higher Olefins	Dimethyl Ether	EO and EG
Tanks, Loading								
Minimising losses	Fixed Roof fitted with internal floating deck		✓	✓				
	Floating Roof fitted with double seals for benzene and ethyl benzene storage		✓					
	All liquids containing C9 & lower olefins are stored in tanks with floating internal covers to minimise vent loss				✓			
	All tanks containing olefin and solvent are nitrogen blanketed above floating internals				✓			
	Vapour recovery for benzene & ethyl benzene loading operations (transport)		✓					
	Nitrogen Blanket to prevent degradation by oxygen ingress - hot oil storage	✓						
	Tanks balanced to header						✓	
	Refrigeration							✓
Safety Systems								
Relief Systems	All HC relief valves go to the refinery flares		✓					
Flare Systems	Flue gases discharged at adequate height for dispersion	✓						
	Designed to minimise local radiation effects	✓						
	Steam used to minimise smoke generation	✓		✓	✓			
	Flammable Gases				✓			✓
	Flammable Liquids				✓			

Table 3.23 Summary of control techniques: Petrochemical Processes (Cont.)

Control Technique		Cumene	Ethyl benzene	Ethylene	Alpha Olefins	Higher Olefins	Dimethyl Ether	EO and EG
Waste Water/Drains								
	All surface water/process drains routed to site effluent treatment plant via gravity separation unit	✓						
	Effluent Treatment Plant outside scope of this authorisation	✓						
	HC drained from vessels, columns and pumps are routed to a closed drain system and the HC collected is routed to refinery slops		✓					
	Closed sewer systems		✓					
Sour water Stripping	Sour water from vessels is drained in a closed system to the sour water system for stripping		✓					
Oil Water separation	Oligomerisation Relief Drum transfers olefin/solvent to storage tank for phase separation				✓			
	General non-process drains - Routed to an interceptor. Any oil is skimmed off and the water allowed to flow to the river				✓			
	Recovery of lube oil and coolants							✓
Segregation	System designed to separate different kinds of water drainage				✓			
	Three closed drainage systems in operation: volatile liquids, high temp waste, large volume waste				✓			
	Two systems are installed for collecting drips and drains, for recovery to process or fuel				✓			
Separation/Recovery	A below grade collection header. Material drained from equipment, sample points, etc. is recovered for fuel use				✓			
	Drains are connected to the Oligomerisation Relief Drum where oligomer and solvent can be phase separated and recovered				✓			
	Other drains are connected to the I/D Relief Drum for recovery to process or to fuel				✓			
Separation/Treatment	Solvent process area - Routed to the CP interceptor. Hydrocarbons are skimmed off. Aqueous phase sent to site chemical plant collection unit & sent to NWW Biotreater at Ellesmere Port				✓			
	non-solvent process area - Routed to the CP interceptor. Hydrocarbons are skimmed off. Aqueous phase sent for biotreatment				✓			
Neutralisation	Lime treatment and settling						✓	

Table 3.23 Summary of control techniques: Petrochemical Processes (Cont.)

Control Technique		Cumene	Ethyl benzene	Ethylene	Alpha Olefins	Higher Olefins	Dimethyl Ether	EO and EG
Ground protection/ Solid wastes								
Landfill	Returned to Mobil, USA as landfill -Alkylation Catalyst		✓					
	Molecular sieve		✓					
	Inert Alumina		✓					
	Stored in 3-walled bunker open to the atmosphere for upto one week - spent isomerisation catalyst, molecular sieve				✓			
	Catalyst Regenerated in situ. One of the catalysts is also sieved to remove fines and reused. Spent solid emissions are sent to registered landfill sites				✓			
	Major quantity of emission to landfill. Reaches landfill as ash from the solids kiln - Alumina				✓			

Table 3.24 Summary of Control Techniques: Acid/Aldehyde Processes

Control Technique		Acetylene	Cellulose Acetate	Formaldehyde (FORMOX)	Formaldehyde (Silver Catalyst)	Phthalic Anhydride from naphthalene	Terephthalic Acid (PTA),	Acetic Acid	Methacrylic Acid	Adipic Acid
Air Emissions										
VOCs										
Design	Offgas from paraxylene reaction passed through a series of condensers & scrubbers to remove paraxylene and acetic acid						✓			
	Solvent Recovery designed to remove water of reaction from acetic acid by distillation before recycling the acid.						✓			
	High temperature alarms to reduce concentrations of VOC in process purges								✓	
Design Standards		✓								
Thermal oxidiser	Purge gas collected in common vent manifold and sent for destruction on the plant thermal			✓		✓		✓		
	Zoned boiler with heat recovery on flue gases.									✓
Recovery to fuel	Directed to a Tail Gas Boiler and burned.				✓					
	Combustion gases pass through waste heat boiler & are exhausted via 15m stack									
	Heavy Organics and light gases used as fuel									✓
Leak Detection	Constant checks on flammability and toxicity of atmosphere	✓								
Refrigeration/ condensation	Crystallisers are equipped with condensers to remove condensables from the vapour before release						✓			
Scrubbing Systems	N-anhydride		✓							
	Use of Amospheric Absorber to remove Acetic Acid vapour from vent stream						✓			
	Organics scrubber to remove organics from column overheads.						✓			
	Various Water/Mineral oil/acid scrubbing systems									✓
	Offgas scrubbed before flare system									

Table 3.24 Summary of Control Techniques:
Acid/Aldehyde Processes (Cont.)

Control Technique		**Acetylene**	**Cellulose Acetate**	**Formaldehyde (FORMOX)**	**Formaldehyde (Silver Catalyst)**	**Phthalic Anhydride from naphthalene**	**Terephthalic Acid (PTA),**	**Acetic Acid**	**Methacrylic Acid**	**Adipic Acid**
Vents	All possible vapour release points routed to vent at safe location above plant building -acetylene	✓								
	All vent lines have 'tell-tales' that feed gas from the vent to a flammable gas detector	✓								
	Acetylene service piping has 1" nitrogen purge vents	✓								
	Height of vent points is such that no personnel, on or off the site, will be exposed to harmful levels of thermal radiation if vented acetylene ignites.	✓								
	Acetylene from cylinders to be tested vented into 0.05 barg LP acetylene system.	✓								
	When a carbide hopper is refilled the residual acetylene in the hopper is vented to the LP acetylene system prior to hopper purging.	✓								
	Vent Gas burner								✓	
Combustion Gases	NOx Catalytic destruction									✓
Tanks, Loading										
Minimising losses	Small quantity vaporises as it is taken from and filled into the storage tanks. No abatement. - Acetone	✓								
	Tanks balanced to header		✓							
	Acetic Acid - Storage vent to Atmospheric Absorber. The absorber is fitted with nozzles to spray liquid in order to condense vapour.						✓			
Safety Systems										
Relief Systems	LP acetylene system protected by a water leg relief device	✓								
	Discharge to high point vent									✓

Table 3.24 Summary of Control Techniques: Acid/Aldehyde Processes (Cont.)

Control Technique		Acetylene	Cellulose Acetate	Formaldehyde (FORMOX)	Formaldehyde (Silver Catalyst)	Phthalic Anhydride from naphthalene	Terephthalic Acid (PTA),	Acetic Acid	Methacrylic Acid	Adipic Acid
Waste Water/Drains										
Drainage	No releases of prescribed/controlled substances to controlled waters	✓			✓					
	Designed to carry away normal rain water and drainage from the blowdown of the acetylene compressors	✓								
	Also carries away drainage from the landscaped slag-heaps which surround the plant, and this from the majority of drainage	✓								
	Treated with lime and settling		✓							
	Discharges are pumped to the on site effluent treatment plant (another authorisation)				✓			✓		✓
Segregation	All liquid waste collected with the plant lime slurry.	✓								
Separation/Recovery	Salts removed from the plant in solid residues are recovered in the residue treatment plant.						✓			
Separation/Treatment	Lime Slurry - Contains 13% solids, with a low settling rate. Currently no water recovered. Slurry removed from site by tanker by specialist materials handling contractor	✓								
	Effluent pit to residue treatment plant						✓			
	Sulphuric acid recovery								✓	
	Recovery of Copper using ion exhange									✓
Site Interceptor	Lagoons						✓			
Containment	Losses due to handling spillages, and plant purges minimised by careful handling. Mn, Co & Br salts						✓			
	Used for corrosion control. Emission release minimised by careful handling.						✓			
	Double mechanical seals on new pumps									✓
	Spill containment tank									✓
Neutralisation	pH monitored and kept in the range of pH 4 - 11						✓			
	Leaks neutralised with Na_2CO_3 (soda ash)						✓			
	Neutralisation to drain						✓			✓

Table 3.24 Summary of Control Techniques:
Acid/Aldehyde Processes (Cont.)

Control Technique		Acetylene	Cellulose Acetate	Formaldehyde (FORMOX)	Formaldehyde (Silver Catalyst)	Phthalic Anhydride from naphthalene	Terephthalic Acid (PTA),	Acetic Acid	Methacrylic Acid	Adipic Acid
Ground protection/ Solid wastes										
Landfill	Consist mainly of coke, with small quantities of silica, iron oxide, alumina and manganese. Disposed offsite by licensed waste disposal contractor.- Generator solids	✓								
	Calcium carbide drums sent to scrap for metal recycling	✓								
	Boron rich organic residues									✓
Special Wastes	Spent purifier catalyst disposed of as a notifiable waste according to special waste regulations	✓								
	Cyclones - Dust		✓							
Catalyst	Catalyst drums collected by drum re-cycling company									
Minimisation	Solids present in vent stream are removed by water sprays in the inlet venturi. The vent scrubber acts as a disengagement drum.						✓			
	Buffer Hopper vented through a mechanical scrubber.						✓			
Filter	Terephthalic powder conveying gas vented via bag filters						✓			
	Solid residues are normally slurried with condensate and pumped to Residue Treatment Plant						✓			
Tank containment	Raw material & product stored in bunded tanks, no high level alarms				✓					

Table 3.25 Summary of control techniques: Sulphur Processes

Control Technique		Sulphenamides	Sulphate and phosphate surfactants
Air Emissions			
Scrubbing Systems	Venturi scrubbing system treats the H_2S and CS_2 off-gases with caustic soda solution before discharging to atmosphere via 16 m stack	✓	
	Volatile/Odorous/Toxic Materials -All reactor vessels vent to common scrubber system: an acid scrubber & water scrubber in series, Sulphonation vessel has an additional scrubber. Effluent flows to wastewater treatment plant. Exhaust flows to main scrubber plant		✓
	Sulphonation vessel has an additional scrubber. Effluent flows to wastewater treatment plant. Exhaust flows to main scrubber plant		✓
	Non Volatile/Odorous/Toxic materials - Vent directly to the water scrubber		✓
Loading and Unloading	Tanks are charged via sealed lines without losses		✓
Relief Systems	Sodium MBT Relief vent at sufficient height to ensure adequate dispersion	✓	
Waste Water/Drains			
Drainage	Discharges are pumped to the on site effluent treatment plant (another authorisation)		✓
Sour water Stripping	Toluene Stripper recovers toluene from the airblowing tanks.	✓	
Segregation	Waste water segregated into weak and strong effluent streams, depending on source and extent of organic contamination	✓	
Separation/Treatment	On-site effluent treatment plant for biological treatment	✓	
Site Interceptor	Emergency storage tanks protect the plant from high flowrates that occur during periods of prolonged, heavy rain	✓	
Containment	Barriers are installed at suitable locations to protect equipment from damage	✓	
	Carbon Disulphide prevented from passing to the drains in the offloading area by a trap fitted with a valve	✓	
	In the event of a spillage the carbon disulphide is contained below a layer of water in the trap	✓	

Table 3.25 Summary of control techniques: Sulphur Processes (Cont.)

Control Technique		Sulphenamides	Sulphate and phosphate surfactants
Ground protection/Solid wastes			
Landfill	General waste to landfill		✓
General Solid Waste	Minimised by recovery or rework as far as possible. Disposal is achieved by off-site disposal via approved facilities	✓	
Special Wastes	Sent for incineration on site.		✓
	Redundant raw materials - Off-site treatment or Incineration,		✓
Dust	Solid raw materials are bought as pellets rather than powder whenever possible		✓
Catalyst	Organic and particulate releases to air during plant cleaning /SRU catalyst replacement minimised by containment in closed drums or kegs	✓	
	Reactor vessels are charged via manhole with the vessel vent open to the scrubber, to provide dust extraction		✓
Recovery	Spent oil collected by recovery company		
	Storage drums sent to drum recovery		✓
Tank containment	Raw material & product stored in bunded tanks,		✓
	Storage tanks located within a concrete bund coated with an expoxy resin for corrosion protection from spilled materials	✓	
	storage not fitted with high level alarms	✓	✓
	Overflow line from each tank is brought down to low level to discharge within the bund	✓	
	Good Manufacturing Practice used to minimise leaks and spills		✓

Table 3.26 Summary of control techniques: Nitrogen Processes

Summary of Control Techniques	Nitrogen Process	Bead Polymerisation	Mono-Nitrobenzene (MNB)	Aniline Process	Mono, di, and tri-methylamine,	Mono, di, and tri-ethylamine, Mono and di-isopropylamine	Amine Related Surfactants	Methyl Aldehydes	Adiponitrile	Acryonitrile	Hexamethylenediamine
Control Technique											
Air Emissions											
NOx	Staged air combustion minimises release of NOx		✓								
VOCs											
Design	Process technology employed to minimise the quantity of by-products		✓								
	Offgases minimised by purifying the hydrogen using a hollow fibre membrane separation system			✓							
	Heavy organics burnt as fuel									✓	
	Recovery by crystallisation/separation of ammonium sulphate									✓	
Design Standards	Use of minimum flanged pipework, canned & double mechnical seal pumps.				✓						
Thermal oxidiser	Purge gas collected in common vent manifold and sent for destruction on the plant thermal oxidiser			✓							
Vents	Highest benzene containing vent is nitrogen padded			✓							
	Vent header vents to flare stack via appropriate scrubbing system (not covered by this application), picks up releases from reactors, tanks and relief valves. System nitrogen purged to minimise oxygen concentrations.				✓	✓		✓			
Scrubbing Systems	Vacuum pump vent scrubbed with nitrobenzene			✓			✓				
	Process vents and offgases are scrubbed using a variety of absorbents, including chilled water and adiponitrile								✓	✓	✓

Table 3.26 Summary of control techniques: Nitrogen Processes (Cont.)

Summary of Control Techniques	Nitrogen Process	Bead Polymerisation	Mono-Nitrobenzene (MNB)	Aniline Process	Mono, di, and tri-methylamine,	Mono, di, and tri-ethylamine, Mono and di-isopropylamine	Amine Related Surfactants	Methyl Aldehydes	Adiponitrile	Acryonitrile	Hexamethylenediamine
Control Technique											
Tanks, Loading											
Minimising vent losses	Tanks balanced to header			✓							
	Benzene tank level controlled to minimise benzene venting		✓								
	Vent System is balanced off with the large bulk tank vent to reduce vapour emissions			✓							
	Where practicable, tanks operated at constant level and temperature to minimise breathing losses			✓							
	Alcohol tanks breath to atmosphere via flame traps					✓					
Loading and Unloading	Transfer by pump to minimise generation of vapour	✓									
	Off-loading facilities equipped with back balancing to the tank to minimise emissions		✓								
	Self-sealing flexes are used to offload tankers into the big nitrobenzene bulk tank.			✓							
	Tanker drive-away protection and over-filling protection			✓							
	Vapour return lines									✓	✓
Containment	Loss of containment guarded against by good engineering design and statutory inspections, Alarms & Trips			✓							
	Anhydrous/Aqueous Methylamine Products - Stored in pressurised tanks that breath, if necessary, to enclosed flare header system.				✓						
	Displaced vapours from tanker filling operations pass through at least one absorber prior to release to atm.				✓						
	Good Manufacturing Practice used to minimise leaks and spills				✓						

Table 3.26 Summary of control techniques: Nitrogen Processes (Cont.)

Summary of Control Techniques	**Nitrogen Process**	**Bead Polymerisation**	**Mono-Nitrobenzene (MNB)**	**Aniline Process**	**Mono, di, and tri-methylamine,**	**Mono, di, and tri-ethylamine, Mono and di-isopropylamine**	**Amine Related Surfactants**	**Methyl Aldehydes**	**Adiponitrile**	**Acryonitrile**	**Hexamethylenediamine**
Control Technique											
Containment (contd)	Ammonia/higher amine storage Tanks - Stored in pressurised tanks. Use of minimum flanged pipework, canned & double mechnical seal pumps.				✓	✓					
	Emergency tank vents - Thermex (heat transfer fluid) fluid discharges via a cyclone.					✓					
Stabilisation	Tanks are blown with air to prevent polymerisation. Air flows kept to a minimum to minimise release to atmosphere	✓									
Safety Systems											
Relief Systems	LP acetylene system protected by a water leg relief device										
	Sodium MBT Relief vent at sufficient height to ensure adequate dispersion										
Flare Systems	Fuel gas injected into flare header, if necessary, to ensure continued fuel supply to flare stack burners.				✓	✓					
	Burns material discharged from the Methylamines, Higher Amines and DMF plants				✓	✓		✓			
	Two flares, one for vents, one for emergencies								✓		
Design Standards	Nitrogen swept to ensure air not drawn into the tanks.			✓							
Waste Water/Drains											
Drainage	No releases of prescribed/controlled substances to controlled waters			✓							
	TOC emissions eliminated by using amine water from exit the NB Extractor as the seal liquid for liquid ring pump			✓							
	Spilled material contained in bund and sucked out for disposal to a licensed waste disposal site.				✓						

Table 3.26 Summary of control techniques: Nitrogen Processes (Cont.)

Summary of Control Techniques	Nitrogen Process	Bead Polymerisation	Mono-Nitrobenzene (MNB)	Aniline Process	Mono, di, and tri-methylamine,	Mono, di, and tri-ethylamine, Mono and di-isopropylamine	Amine Related Surfactants	Methyl Aldehydes	Adiponitrile	Acryonitrile	Hexamethylenediamine
Control Technique											
Separation/Treatment	Consists of a strong effluent decanter to remove free organic from the aqueous waste stream and a Thermal Oxidiser (TO)		✓								
	Reed bed treatment system, discharging to river, or direct to site drain - Discharge from scrubbing systems,Blow Downs,Vessel/Tank internal washwaters.Bund Draining				✓	✓		✓			
	Process heavy ends sent direct for incineration					✓					
	Bio treatment plant								✓		✓
	Recovery by crystallisation/separation of ammonium sulphate									✓	
	Recovery of cadmium by precipitation with sodium hydrogen sulphide								✓		
Monitoring	Losses from pumps etc. will be detected by TOC analyser and sent for treatment.				✓	✓					
Containment	Good Manufacturing Practice used to minimise losses				✓	✓	✓				
	Use of appropriate engineering standards				✓	✓					
	Use of plant trips and alarms				✓	✓					
Stripping	Amine stripper - Dissolved nitrobenzene, nitrophenols and remaining organics removed from water, which is then sent to drain.			✓							
Aqueous Effluent	Nitrobenzene extractor used to minimize TOC in the amine water (principally aniline). Guards against feeding free organics to the column, for which it is not designed.			✓							

Table 3.26 Summary of control techniques: Nitrogen Processes (Cont.)

Summary of Control Techniques	Nitrogen Process	Bead Polymerisation	Mono-Nitrobenzene (MNB)	Aniline Process	Mono, di, and tri-methylamine,	Mono, di, and tri-ethylamine, Mono and di-isopropylamine	Amine Related Surfactants	Methyl Aldehydes	Adiponitrile	Acryonitrile	Hexamethylenediamine
Control Technique											
Ground protection/ Solid wastes											
Landfill	All to Landfill		✓								
	general waste to landfill			✓							
Special Wastes	Spent filters, disposed of by a licensed waste disposal contractor.			✓							
	Waste material - Drum stored in specially constructed area awaiting disposal via licensed contractors. Area covered by authorisation				✓	✓					
	Some process byproducts are recovered for incineration						✓				
Dust	Dust in filters cleaned up by industrial vacuum cleaners to ensure high standards of hygiene			✓							
	Cyclones - Dust										
Catalyst	Catalyst drums collected by drum re-cycling company			✓							
	Catalyst life is maximised by careful control of operating conditions					✓					
	Residues containing spent Aniline catalyst sent to Off-Site incineration			✓							
Recovery	Spent oil collected by recovery company			✓							
	Heavy/light hydrocarbons recovered and burned in site boilers										
Storage/transfer areas	Nitrobenzene transfer carried out in bunded area to contain spillages			✓							
	Raw material & product stored in bunded tanks,		✓								
	storage not fitted with high level alarms	✓	✓								
	Stainless Steel Storage Tanks, filled to 90% only	✓									

Table 3.27 Summary of control techniques: Monomers and Polymers

Control Technique		EDC/VCM	PVC	Butyl Polymers	Styrene	Styrene Rubber	Polystyrene	Methyl Methacrylate	Acrylic Sheet	Nitrile Rubber	LDPE	Polypropylene	Polyester	Polyester Resins
Air Emissions														
NOx	Low NOx burners with staged-air or staged-fuel systems, coupled with good combustion control to minimise excess air to the burners.			✓	✓									
CO_2	Calorific value of the flue gas recovered by raising steam. Energy efficiency results in 'net' reduction in CO_2 emissions	✓												
Combustion Gases	Controlled by on-line monitoring of the oxygen in the stack gases using a zirconia probe. Oxygen levels are maintained >2% or <5.5% to avoid inefficient burning of fuel	✓												
	Flue gas of burners monitored for unburnt methane and HCl. If unburnt HCl detected, indication of leaking cracker tube.	✓												
Boilers	Almost exclusively operated on a natural gas basis						✓							
HCl sampling	Anhydrous HCl rarely sampled due to high pressure, low temperature	✓												
Safety Systems														
Flare Systems	Flue gases discharged at adequate height for dispersion			✓							✓	✓		
Loss of Containment	Spillages from VCM storage pumps are directed to a shallow containment/evaporation area well away from the pumps which could provide ignition source	✓												

Table 3.27 Summary of control techniques: Monomers and Polymers (Cont.)

Control Technique		**EDC/VCM**	**PVC**	**Butyl Polymers**	**Styrene**	**Styrene Rubber**	**Polystyrene**
VOCs							
Sampling	Sampled via fast loop system	✓					
	VCM sampled using of in-line bombs or sample syringes	✓					
Leak Detection	VCM emissions monitored by On-Line Multipoint Analysis system	✓					
	Areas handling these chemicals are fitted with flammable gas detectors VCM, Ethylene, EDC	✓					
Organic Vapour	Daily checks of the plant roadways are made with an Organic Vapour Analyser (OVA) meter	✓					
Vents	Fitted with variety of condensers, scrubbers and filters	✓	✓				
	Vents released to atmosphere via tall stacks	✓	✓				
	VCM shipping vent is back balanced to the VCM sphere to prevent any losses to atmosphere	✓					
	EDC shipping vent line is fitted with a liquid knock out pot to recover EDC droplets entrained in the vent gas	✓					
Refrigeration/ condensation	Lights vent fitted with a cooling water condenser to lower vent gas temperature. EDC removed in knock-out drum	✓					
	Heavies vent fitted with an EDC contact condenser to scrub HCl and EDC from the vent stream	✓					
Scrubbing Systems	Direct chlorinator vent gas is scrubbed with caustic to remove all trace quantities of chlorine	✓					
	EDC stock tank vent fitted with a vent gas scrubber to absorb HCl	✓					
	Flash drum recovers organics from the oxy effluent stream during times of stripper unavailability	✓					
Fume Scrubber	Monitored visually. Cleaned as required on shutdown						✓

Table 3.27 Summary of control techniques: Monomers and Polymers (Cont.)

Control Technique		EDC/VCM	PVC	Butyl Polymers	Styrene	Styrene Rubber	Polystyrene
Tanks, Loading							
Minimising Breathing	External Floating Roof			✓			
	VCM storage vents to PVC plant for recovery	✓					
Loading and Unloading	Carried out in a manner to minimise losses to ground or atmosphere	✓					
	overfill protection				✓		
Monitoring	Monitored annually						✓
Waste Water/Drains							
No treatment	Cooling Water purge, Decoke pit overflow, weak acid pit overflow	✓					
Drainage	Effluent Treatment Plant outside scope of this authorisation	✓					
Oil Water separation	Phase separator allows free phase EDC, in the batch-wise effluent stream, to separate and settle out	✓					
	Sent through an oil/water separator which will remove free phase oil	✓					
	EDC drain and wash liquors - During routine maintenance, liquor is routed to an EDC recovery pit to recover free phase organics to the process	✓					
Segregation	Lagoons					✓	
	Procedures are in place to allow diversion of 'out of consent' surface water drainage.	✓					
	stormwater and surface run-off flows to an oil/water separator, prior to discharge to Sewage Works						✓
	Contaminated drainage - to interceptor pit, to recover free phase organics	✓					
	Filters					✓	
Site Interceptor	Receives all water from process and storage areas is subjected to daily visual inspection for oil/HC contamination						✓
Stripping	Stripping of chlorinated organics from wastewater	✓	✓				
Monitoring	TOC of outlet stream continually monitored. Monitoring equipment checked on daily basis.						✓

Table 3.27 Summary of control techniques: Monomers and Polymers (Cont.)

Control Technique		EDC/VCM	PVC	Butyl Polymers	Styrene	Styrene Rubber	Polystyrene
Ground protection/ Solid wastes							
	No systematic direct releases of prescribed substances to land						✓
Landfill	Part polymerised material is removed for sampling. Stored in drums and disposed to licensed landfill sites.						✓
	Sent off-site to landfill	✓	✓				
	Solid waste disposed of to licensed waste disposal facilities						
	All wastes released to land are disposed of at licensed waste disposal sites by licensed contractors.	✓					
	Removed to licensed landfill, e.g. packaging material, used filters and wipes, PMMA residues not suitable for recycling						
Separation/Recovery	Organic Residues - Sent to Per/Tri plant for recovery of useful organics, or sent for borehole disposal						
Minimisation	Oxy-reactor fitted with internal cyclones to minimise the loss of catalyst particles with the product gases	✓					
	Used catalyst from a sister VCM plant is used as top-up catalyst on the VC3 process.	✓					
	Solids in de-coke effluent are allowed to settle in a de-coke pit before the effluent overflows to site outfall drainage system	✓					
	Majority of solid waste is recycled via saleable disposal						✓
Containment: tank area	Bunded to contain forseeable spillages						

Table 3.28 Summary of control techniques: Monomers and Polymers (2)

Control Technique		Methyl Methacrylate	Acrylic Sheet	Nitrile Rubber	LDPE	Polypropylene	Polyester	Polyester Resins
Air Emissions								
VOCs								
Design	Polyester reaction carried out with a nitrogen gas atmosphere.						✓	
Thermal oxidiser					✓	✓		
Refrigeration/ condensation	Glycol/water coolant is widely used in vent condensers to reduce releases of volatile organics into air	✓						
	Distillation column fitted with a glycol/water-cooled back-up condenser to minimise vent emissions from the distillation.	✓						
	Vent gases collected in a series of vent headers and directed toward a Vent Gas Burner where they are incinerated.	✓						
	Steam ejector vents condensed against cooling water which is circulated via a cooling tower.	✓						
	The still vent condenser is refrigerated to minimise emissions of HCN	✓						
	Water cooled condensers on the process vessels at or below atmospheric pressure						✓	
Scrubbing Systems	Contents circulated continuously through glycol/water-cooled chillers.	✓						
	Vent on reactors scrubbed with incoming acetone feed to remove HCN	✓						
Cooling Towers	Induced draught cooling tower fitted with drift eliminators to minimise losses		✓					
Fugitive emissions	Minimised by effective training of operatives, maintenance & inspection routines, etc						✓	
Tanks, Loading								
Minimising Breathing	Some by-product acid tanks are open topped. A tar layer forms on the top which has to be removed by crane grab occasionally	✓						
	Stock tanks are fitted with conservation vents to minimise breathing losses.	✓						
	Balancing line			✓				
	Process stabiliser mixing and distribution tanks are back balanced to each other to eliminate emission of MMA laden vapour on transfer	✓						

Table 3.28 Summary of control techniques: Monomers and Polymers (2) (Cont.)

Control Technique		Methyl Methacrylate	Acrylic Sheet	Nitrile Rubber	LDPE	Polypropylene	Polyester	Polyester Resins
Loading and Unloading	Carried out in a manner to minimise losses to ground or atmosphere							
Final product cooling	The exiting final product is cooled to reduce the storage temperature and thereby reduce emissions	✓						
HCN	Vent on HCN import storage tank scrubbed with caustic solution.	✓						
	Methanol Storage Tanks are purged with N_2 via breather valves fitted to the vent line. Breather valves exhaust to the atmosphere.	✓						
	Breather valves from underground acetone stock tanks and mixing tank are purged with N_2 and exhaust to atmosphere	✓						
	Return vapour line for filling. No vent on stock tank - catalyst	✓						
	High Level Alarms prevent overflow of tanks, and on particularly critical duties trip systems also prevent overflow	✓						
Stabilisation	Product tanks require the presence of air to activate the chemicals used to stabilise the product.	✓						
	Unstabilised MMA storage are cooled to keep MMA at 0°C, to reduce vent losses	✓						
Other	Fitted with pressure and vacuum relief valves		✓					
	System of work in place to minimise releases from the styrene storage tank							✓
	New tank for the bulk storage of maleic anhydride, to minimise emissions to the atmosphere							✓
Safety Systems								
Relief Systems	Designed to operate as a last resort to minimise releases to atmosphere		✓					
Flare Systems	Flue gases discharged at adequate height for dispersion				✓	✓		
Reaction Vessels	All pressure vessels designed to withstand an internal explosion or runaway reaction		✓					
	Protected by a stack with two bursting disc in series		✓					

Table 3.28 Summary of control techniques: Monomers and Polymers (2) (Cont.)

Control Technique		**Methyl Methacrylate**	**Acrylic Sheet**	**Nitrile Rubber**	**LDPE**	**Polypropylene**	**Polyester**	**Polyester Resins**
	Fitted with condenser and knock-out pot to reduce quantity of vapour and liquid droplets emitted during venting		✓					
Loss of Containment (safety systems contd.)	Spillages from VCM storage pumps are directed to a shallow containment/evaporation area well away from the pumps which could provide ignition source							
Loss of Containment	All potentially open ends on the plant have beed identified	✓						
	All pipelines containing strong HCN outside cubicles are registered and are of all welded construction	✓						
	The plant is maintained to a high standard	✓						
Waste Water/Drains								
Drainage	There is no on-site effluent treatment plant. Drainage system discharges into local sewerage system						✓	
	There is no direct release from the process to water						✓	
	Treated prior to consented discharge		✓					✓
Segregation	Water that may contain MMA or oil is collected in separation pits to prevent water contaminated with non-solubles draining to sewer		✓					
Separation/Recovery	Liquid By-product Acid (BPA)-Disposed of to a sulphuric acid recovery plant	✓						
Separation/Treatment	Aqueous effluents containing HCN are treated at the sodium cyanide effluent treatment plant.	✓						
	TOC - Organic recovery unit removes some organics from By-product acid before discharge.	✓						
	Acidified ammonium sulphate solution will eventually go to ammonium sulphate recovery, although is currently released to outfall.	✓						
	Polyester polyols too high in COD for discharge. Tankered away to Water treament						✓	

Table 3.28 Summary of control techniques: Monomers and Polymers (2) (Cont.)

Control Technique		Methyl Methacrylate	Acrylic Sheet	Nitrile Rubber	LDPE	Polypropylene	Polyester	Polyester Resins
	Ammonia/water mixtures from the ammonia vaporiser are stripped by heating to remove the ammonia	✓						
	Some aqueous effluent pumped to the plant furnace for destruction by burning of any organic present.	✓						
	Chemical treatment			✓				
Monitoring	The still bottoms acidified water purge is continuously monitored for HCN	✓						
	Trip systems prevent HCN escaping in the acidified ammonium sulphate stream	✓						
	The consented discharge is continuously monitored	✓						
Containment (aqueous sytems)	All operations employing liquid HCN or concentrated solutions containing HCN are handled in cubicles	✓						
	Cubicles are ventilated buidlings built to contain any spillages or leaks. Vapours are extracted by a fan and vented high to atmosphere	✓						
	HCN cubicle is provided with a secondary containment pit, processed via the sodium cyanide plant effluent treatment system.	✓						
	Waste solvent stored in steel drums in Polyol drum area						✓	
Neutralisation	Neutralised and discharged to the river.- Weak acid sump discharge	✓						
	Adds sodium hydroxide to convert any HCN present into sodium cyanide	✓						
	Normally a significant quantity of acidified still bottoms water is recycled for further process use.	✓						

Table 3.28 Summary of control techniques: Monomers and Polymers (2) (Cont.)

Control Technique		**Methyl Methacrylate**	**Acrylic Sheet**	**Nitrile Rubber**	**LDPE**	**Polypropylene**	**Polyester**	**Polyester Resins**
Ground protection/ Solid wastes								
	No direct release from the process to land						✓	
Landfill								
Solid waste	Sent to licensed waste disposal facilities	✓						
General Solid Waste	Removed to licensed landfill, e.g. packaging material, used filters and wipes, PMMA residues not suitable for recycling		✓					
Special Wastes	Packaged for disposal or recovery off-site by a licensed operator/waste disposal company. Generally incinerated.		✓					
Minimisation	The choice of catalyst eliminates the disposal of catalyst salts to land	✓						
	Drier vent on ammonium sulphate plant passes through a dry cyclone and wet scrubber to remove ammonium sulphate dust.	✓						
	Process stabilisers employed to minimise the formation of solid polymer and tars.	✓						
Filter	Dusts				✓	✓		
Packaging Waste	All 45 gals storage drums are recycled through a registered drum cleaner/recycler						✓	
	All raw material storage sacks, paper, plastic are compacted into skips for disposal at a registered landfill site.						✓	
	Wooden pallets are removed by a pallet recycling company						✓	
Unsaleable waste	Process allows for correction of the product to specification before discharge and						✓	
	Process allows for reblending of off-specification product into future batches.						✓	
Unsaleable stock	Disposed of by licensed contractors for landfill or incineration							✓
Containment: tank area	All storage tanks bunded to take the full tankcapacity	✓	✓					
	Bunded to contain forseeable spillages		✓					
Noise	Silencers and good design to reduce noise both at the site boundary and within the plant		✓					

- Organics in displaced vents from tanks or loading are destroyed or removed in some instances. Examples include vapour recovery on loading operations for benzene and ethylbenzene, aqueous scrubbing of acetic acid from storage tanks and amines from tanker loading. Scrubbers may also be fitted for inorganic pollutants, such as HCl from EDC (ethylene dichloride storage) or HCN on methyl methacrylate storage.

- Tanks on some plants have only a pressure relief breather that vents to atmosphere, while some other plants appear to have little abatement from tanks or loading operations even when relatively volatile organics are handled.

Fugitive emissions

- High integrity design features are quoted for methylamines, for example, including minimisation of flanges and the use of dual mechanical seals. Additionally, blanking and capping of drains and vents, loop systems for sampling, and low leak valves are quoted for ethylbenzene. Odour (methylamines) and toxicity (benzene) may be drivers in these particular cases.

- Leak detection on a six-monthly basis is cited for acetylene production.

- Analysers are installed in the compressor house (alpha olefin production) to detect ethylene leaks; this also has safety implications. Flammable gas detection is noted elsewhere also. Similarly, continuous VCM measurement is important for occupational health reasons.

- Drainage systems from equipment are usually enclosed.

- A low level of fugitive abatement measures is reported in the IPC documentation, but this may be misleading. The issue of general VOC control has gained prominence comparatively recently and some companies are known to have instigated their own programmes in the last few years.

Intermittent emissions

- A site flare system is often (but not always) available for intermittent releases such as from pressure relief valves or on start-up or shut-down. Design features of the flares include discharge at adequate height, supplementary fuel supply and the use of steam to minimise smoking.

- Relief pressures are set high enough to minimise unnecessary venting.

Continuous vents

- Thermal oxidisers are used in several instances on, for example, phthalic anhydride purge gas, formaldehyde tail gas, aniline purge gas, vent gases from methyl methacrylate and polyolefin purges, acetic acid, formic acid and propionic acid

- Control by vent condensers includes water-cooled units (EDC/VCM) and chilled glycol cooling (methyl methacrylate). A refrigerated still vent is used on methyl methacrylate production to control emissions of HCN.

- Scrubbing in aqueous solutions is a common control technique. Examples include removal acetic acid from vents, or caustic scrubbing to remove CS_2 and H_2S on sulphenamides production.

- Scrubbing by organic absorbents is less common, except within the normal process recovery loops. An example of end-of-pipe treatment of this sort is the scrubbing of a vacuum pump vent with nitrobenzene on the aniline process.

- A membrane separation system is used to purify hydrogen to minimise aniline process off-gases.

Minimisation and recycling

- Where an organic material is used as a solvent, there may be possibilities to substitute it for another with a lower vapour pressure or of lower environmental impact. A change from toluene to p-tertiary butyl toluene on alpha olefin production is an example.

- Recycling may require process-specific measures, for example distillation of acetic acid in terephthalic acid production.

- Specific process technology variants may minimise the quantities of by-products. The aniline process used by ICI is cited as an example.

While VOC emissions are the most frequently addressed form of atmospheric pollution, abatement techniques are reported also on other types of emission to air.

- Low NOx Burners are used in several plants.

- Thermal oxidisers are used to control significant emissions of carbon monoxide, such as on ethylbenzene and phthalic anhydride processes.

- Scrubbing with aqueous solutions is a common control technique for soluble inorganic pollutants or those that react with a soluble reagent. Examples include scrubbing of HCl from EDC (ethylene dichloride) stock tank vent, and of chlorine (with caustic) from EDC direct chlorinator vent.

3.4.3 Techniques to control emissions to water

- Because wastewater treatment is usually conducted on a site basis, rather than for each process plant, the abatement techniques for aqueous effluents are often not reported in applications/authorisations for the processes reviewed here. Techniques typically used in site wastewater treatment are not included in the following notes.

- It is standard practice to collect aqueous effluents from process sources, including the drainage or washing out of equipment, and send to proper disposal. The same applies to stormwater or external wash water in areas where contamination is possible.

- Segregation of waste waters is also common. Process wastewater typically passes directly to appropriate treatment, while water that would usually be uncontaminated is often directed to an interceptor to remove any oily phase before discharge to surface water. Process wastewater is also segregated into different categories, such as strong and weak effluent, at some plants.

- Analysis is used on some plants (e.g. methylamines) to detect leaks from machinery or fittings and permit them to be directed to treatment.

- Some (usually concentrated) wastes are collected in a basin or pit before being taken from the site for treatment as a special waste, rather than being mixed into the site effluent stream. These might include spilled material, such as in methylamines production.

- Buffer capacity is available at some plants mainly in the form of lagoons or basins, both to provide a means of controlling feed to common wastewater treatment and to permit the quality of treated wastewater to be checked before discharge. This is used in particular when the plant effluent is difficult to treat or contains pollutants of particular environmental sensitivity.

- Plant-based phase separation is common. It aids re-use of the organic phase on the producing plant as well as cleaning the effluent before piping elsewhere.

- Strippers are common on-plant treatment devices, permitting recycle of the stripped component and preventing it degassing in downstream treatment facilities. Examples include sour water stripper (e.g. ethylbenzene), amine stripper (nitrobenzene/aniline), and ammonia stripper (methyl methacrylate).

- Neutralisation is also performed at the plant where appropriate, such as neutralisation of leaks with soda ash on terephthalic acid production, or with caustic on methyl methacrylate.

- Thermal oxidation is used for some aqueous effluent streams with components that would be difficult to treat adequately in conventional site wastewater treatment systems. Selected process streams on nitrobenzene production and methyl methacrylate production are treated by thermal oxidation, for example.

- On-plant recycling can take the form of use of weak aqueous organic streams for process purposes, such as amine water used as liquid ring pump seal on aniline production.

3.4.4 Land wastes and ground protection

Production and disposal of wastes

Wastes from petrochemical and large scale organic processes are mostly reported as being sent to disposal by approved routes. This includes the return to vendor of spent catalysts or other process beds, recycling of used oils and drums via specialist contractors, and disposal of special wastes to landfill, treatment or incineration by qualified contractors.

Particular topics of interest are examples of minimisation or recycling of wastes, and of special on-site treatment. Catalyst selection is cited as a method of reducing formation of by-products, such as catalyst salts. Careful operation is a means of extending catalyst life. Blending of off-specification material back into the commercial product is another means of reducing waste quantities, in addition to the obvious economic benefit.

By-products can be recycled for re-use in some cases, such as chlorinated wastes from EDC production passing to solvent manufacture. It should be noted that the alternative disposal route for these materials in the case examined is quoted as to borehole, rather than the on-site incineration and HCl recovery that is common outside the UK. The use of borehole disposal is unlikely to be tenable for such materials.

Ground protection

Proper disposal of land wastes is necessary to protect soil and groundwater from contamination. Another important element is the containment of any leaks or spills from tanks, on loading/unloading, or from other operations. Techniques include the use of impermeable linings, such as coated and impregnated concrete, on the floors of tank bunds and transfer stations. This is not universal practice. Measures to prevent overfilling of tanks are mentioned in Section 3.4.2 above.

3.5 Release limits

Release limits expressed as concentrations are often not quoted on authorisations, particularly if the emission is intermittent or fugitive. Examples of current target release level concentrations are shown on Table 3.29 and data noted from the authorisations reviewed, where possible, are summarised on Table 3.30.

Table 3.29 Achievable release levels for emissions to air: examples from current guidance notes

Pollutant	Release level (mg/m^3)
	10
Ammonia	15
Benzene	5
Carbon disulphide	5
Chlorine	10
CO	100
EDC	5
Formaldehyde	5
HCl	10
H_2S	5
Mercury	0.1
NOx as NO_2	300
Organic sulphides & mercaptans (expressed as methyl mercaptan)	2
Particulates	20
Trimethylamine	2
VCM	5
VOCs "Class A"	20
VOCs "Class B" (expressed as toluene)	80

Table 3.30 Examples of authorised UK release limits (mg/m^3)

	Storage Tanks	Reactor	Mixers	Ventilation Scrubber	Dryer Cyclone Exhaust	Catalytic Incinerator
Acetic Acid	200			30, 105		
Acetic Anhydride	1 350					
Benzene	2 000			25, 90, 135, 3 000		
Methanol				1 500		
Methyl Acetate				160 000		
Particulate Matter				20	700	
Toluene				1 400		
H_2S	5					
SO_2		130 000	250 000			400
NO_2		400, 1600				350
CO		20 000,100				1 800
VOC		35 000	2 500	300, 20 “A”	and 80 Total VOC	
Amines				20		

	Distillation Column Vent	Relief Header Vent	SRU Tank Vent	Carbon Bed Exhaust	Plant Tail Gas Vent	Plant Cubicle
Acetic Acid	30 000	3 400				
Acetic Anhydride						
Benzene	1 500	100				
Formaldehyde					700	
Methanol	1 500	100				
Methyl Acetate	125 000	5 000				
Methyl Bromide		275				
Toluene	1 500	100		800		
H_2S			1 100			
HCN						10, 130, 250
VOC						170, 290

It is clear by inspection that many of the limits quoted in the authorisations are substantially in excess of those regarded as achievable. Although the mass emissions are omitted for clarity, Chem Systems can confirm that mass emissions exceed the five tons per year cut-point applying to Class B VOCs. In some cases, the emissions are from continuous vents and so there is probably scope for abatement. Where releases are intermittent, such as from tank vents, there might be a technical or economic reasons case to suggest a different limit.

3.6 Topics for further review

The consideration of UK petrochemical and large scale organic processes suggests a number of pollution sources and abatement techniques on which the international review of abatement practices should focus. For most types of source, there are examples of application of techniques of high effectiveness on UK plants. One of the questions is therefore the extent to which these techniques may be expected to apply to all relevant UK plants.

The relevant topics are as follows:

VOCs to air

- Losses from tanks and on transfer.
- Continuous releases, such as from process tail gas.
- Intermittent releases, such as from pressure relief systems.
- Fugitive losses.

Other atmospheric emissions

- Combustion gases.
- Others, such as soluble inorganics.

Aqueous effluents

- Specialist techniques for difficult or high impact pollutants.

Landwastes and ground protection

- Specialist techniques for difficult process-specific wastes.
- Containment techniques to prevent losses to soil or groundwater.

These subjects are addressed in Section 4, which includes a review of techniques used on plants outside the UK and a more detailed examination of selected abatement techniques.

In addition to generally applicable techniques, there are instances where the optimum abatement solution is specific to the particular process. Opportunities for minimisation at source or recycle of waste streams often fall into this category. Chem Systems has therefore examined a selection of six processes or groups of processes to illustrate the solutions that might be applied to individual processes. This review is presented in Section 5, and covers the following processes:

- Formaldehyde, produced by atypical processes, and often linked with downstream resin production on a medium to small scale.

- Polyolefin production, a cornerstone of commodity polymer business, with potential releases of relatively photochemically active olefins.

- EDC/VCM/PVC, which has particular pollution concerns relating to vinyl chloride and other chlorinated organics.

- Adipic acid production, a complex process with particular abatement requirements for nitrous oxide emissions.

- Nitrobenzene/aniline, where there is an intractable aqueous waste that different producers tackle in different ways.

- Emulsion polymers – taking vinyl acetate polymers as an example – as an example of a smaller scale process with batch processing.

4. REVIEW OF ABATEMENT TECHNIQUES

4.1 General

There is a very wide range of techniques that can be used to abate pollution from the sources identified in Section 3.

- The techniques are reviewed below in two ways. Firstly, an extensive list of possible techniques is given. For each technique, or group of techniques, a very brief description is given, with examples of processes in which it is known to be used. This addresses the question of what techniques are best practice in commercially operated plants.

- Secondly, in Section 4.3, selected techniques are reviewed in greater detail, with indications of technical applicability and economics where available.

The Environment Agency rightly emphasises the importance of minimising pollution at source and of recycling material within the process in preference to end-of-pipe abatement. While general comments are included on these topics, the technical possibilities are often very process-specific. In addition, generic abatement techniques can not necessarily be applied to all processes. For these reasons, a number of processes with atypical abatement requirements are reviewed separately, in Section 5.

4.2 Review of techniques used world-wide

A wide range of techniques for reducing emissions is available to operators of petrochemical and large scale organic processes. This section of the report identifies around 150 techniques, or variants of techniques, that technical literature and industry contacts suggest could be applied to the subject processes. While all the techniques are technically feasible in suitable circumstances, they represent a range of applications and performance so are not necessarily BAT in every case. International process operators and equipment manufacturers have been interviewed, using the list of techniques as a checklist. Several of the operators are integrated with refinery operations and use petroleum products such as naphtha as feedstocks; there is some commonality between the subject processes and refining in the techniques used.

As a result of the review, the following information is provided where possible:

- a brief description of the technique
- where the technique is known to be applied
- an indication of the removal efficiency or other performance indicator.

It is implicit in this analysis that many of the techniques are broadly applicable to several processes. A technique is not restricted to the examples identified of processes where it is used.

4.2.1 VOCs to air

Sources of VOCs can be broadly classed as point source emissions; including process vents, tanks and storage, relief and blowdown systems, and non-specific sources such as fugitive leaks and evaporation from water sources.

Techniques to reduce point source emissions of VOCs depend on the concentration of the VOC, the type of compound, and the level to which it must be reduced. Table 4.1 lists examples of abatement techniques currently available or in use.

Table 4.1 VOC abatement technique review

Technique	Plants/Applications	Targets/ Performance	Comments
Tanks/Storage and Transfer			
External floating roof	Examples: often on petroleum based feedstocks Xylenes , Naphtha, Gasoline – Total Benzene – DSM Naphtha – Borealis	70-90% reduction	Regular inspection of seal required. Typically applied to hydrocarbons with flash points less than ambient conditions.

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Secondary seal on floating roof	Not as widespread e.g. ethylbenzene e.g. Total	95% compared to fixed roof	Required on gasoline terminals, not usually mandatory elsewhere
Fixed Roof with internal floating roof retrofitted	Xylenes , Naphtha, Gasoline – Total Alpha olefins	70-85%	C_9 or lighter is one criterion on one plant
Insulation from ambient changes: white paint, thermal insulation	Various - Dow		Dependent on volatility of the stored chemical
Cooling of tank inlet stream	e.g. methyl methacrylate		
High temperature alarm	Widespread		Usually for safety reasons
Warm water/oil tank heating: better control than steam coils; reduced overheating/losses	Volatile hydrocarbons with freezing points above ambient - Dow		Good for products susceptible to heat degradation.
Overfill protection: level measurement, independent high level alarms, high level cut off, batch metering	All: widespread practice		Level control used on some plants to minimise level change during operation.
Pressure/vacuum valve on tank vent: reduces losses on diurnal temperature change	Widespread practice on volatile liquids		
Inert gas blanket and bleed	Widespread but not universal		Usually intended to reduce explosion risks but also reduces volume of tank vent stream in these circumstances

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Tank vapour balance lines		Up to 75%, depending on the application.	Can be applied to intermediate storage tanks, when one level tends to rise as the other falls and there are no contamination problems.
Vapour balance lines: loading systems	Benzene, TDI, pesticides, chlorinated solvents – Dow		
Tanker drive away protection: barriers and interlock systems, self sealing hose connection.	All: widespread practice		On loading/unloading systems
Bottom filling or below surface filling of road or rail tankers	Widespread practice, particularly for volatile petroleum-based materials		
Fixed roof tank with vent to a condensing system	Examples VOCs - ARCO	95%+	
Carbon Adsorption on fixed roof tank vents	Benzene - Total TDI, Epichlorohydrin - Dow	95-99%	Carbon typically disposed offsite. Not suitable for compounds that react exothermically in activated carbon such as ketones, aldehydes amides and dienes.
Regenerative Carbon Adsorption units for loading systems	Gasoline terminals - John Zinc Benzene, gasoline – Total	99% + Recovery down to 35 g/m3 in the vent gas (feed has 30-40% VOC by volume)	Dual bed systems designed for high vapour concentrations. Recovery of hydrocarbons is achieved by vacuum desorption, followed by condensation and recovery of the hydrocarbon to storage. Not suitable for aldehydes, ketones, amides and dienes, which react exothermically with the carbon.

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Common tank vent to:			
a) Flare	Especially with toxic hydrocarbons	98%	
b) Thermal Oxidiser	All VOCs - BASF Benzene from fixed roof tanks – DSM	99.9%+	
c) Refrigerated condenser	All VOCs Pyrolysis gasoline storage at cracker plant - (Borealis Finland)	90 to 99.99%+	Efficiency depends on limits set for the release, the size of the facility and location factors
d) Recovery to process	e.g. VCM		
Minimisation of inventory	Not widely identified as a technique		Economics is the main driver
Controllable Vents – process vent streams containing organics			
High release point to achieve acceptable ground level concentration	Universal practice, but not necessarily sole measure		
Use as a process fuel	Many hydrocarbon process offgases e.g. dissolved ethylene in polyethylene from high pressure process. Ethylene produced on pressure let down is used as plant fuel in some plants	98 - 99%	May need some pretreatment such as demisting/knockout pots. Membranes may also be used to selectively recover components such as hydrogen.
Thermal Oxidation	Large volumes of VOCs or those difficult to biodegrade Examples: Vent gas incinerator on VCM/PVC - Norsk Hydro and EVC Tarex for explosive waste gases – Bayer Purges from LDPE/PP processes	99%+	See Section 5 on EDC/VCM/PVC
Thermal Oxidation (flameless)	Pesticides – Dow Aldehydes and ketones - Quest	99.9%+	Can suit small flows from batch plants; one operator describe a black box of pebbles heated to 1100°C by natural gas.

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Catalytic Oxidation	Formaldehyde, methanol, ammonia, CO, xylenes, benzene, methyl bromide, styrene. Flows from 15 to 70 000 Nm3/h Vapours from aromatics storage e.g. benzene, cumene, phenol	99.9%+	Preheat 200-400°C, recover heat from flue gas. Catalyst poisons include heavy metals, sulphates, and silicone. Also, halogens form acid gases which need scrubbing/ further treatment.
Membrane Recovery	Light hydrocarbons from reactor offgas Example – hydrogen and methane from the aniline process Concentration of VCM or other chlorinated streams - plants in USA	60-90%	Basically a separation and concentration process; may be used in conjunction with condensers
Absorption (organic): Absorption-desorption or absorption and use of laden absorbent as fuel	Few specific examples quoted for petrochemical and large organic plants; examples: PTA process, VCM vent treatment Used for vapour recovery on gasoline loading facilities; quoted uses in fine chemicals/pharma	95%+	
Absorption (aqueous): Scrubbing plus stripping and recovery or plus water treatment	VOCs – ARCO Amines, acids and chlorides – Total Acetic acid and other soluble oxygenates	95% + or to below the smell threshold	Requires appropriate back up systems and alarms.
Carbon Adsorption Fixed bed	Benzene	95-99%	

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Carbon Adsorption: Injection into vent gas	No examples identified		Technique used in particular on incinerator flue gas
Zeolite Adsorption: Pressure Swing Adsorption/ Temperature Swing Adsorption		95-99%	
Adsorption-desorption to concentrate, followed by incineration or recovery	No examples identified on petrochemical-type plants		Suitable for very lightly loaded air streams such as from some coating operations etc.
Indirect condensation: against water or brine	e.g. water cooled condensers on VCM e.g. chilled glycol cooled condenser on MMA	70-90%	Performance usually insufficient for regulatory requirements
Indirect Condensation using – Liquid Nitrogen vaporisation or Closed loop refrigeration cycles using standard refrigerants (e.g. ammonia, ethylene, propylene etc.)	All hydrocarbons, often used for solvent recovery Continuous as well as intermittent vents. Single streams or commoned systems.	20 – 99.999% Removal is dependent on inlet concentration and the vapour pressure of the removed component at the chilling temperature.	Packaged units utilising the cold available in liquid nitrogen stored for supply gaseous nitrogen to the plant can be a good way of recovering VOCs from a wide range of vents. May be more difficult to justify on a large site where gaseous nitrogen is already available. If refrigerants are already available on the plant, these may also be utilised to condense VOCs.
Inert gas drying or other process systems Change from air to nitrogen allows higher organic concentrations (no problems with explosive limits). This enhances the solvent recovery via indirect condensation. Liquid nitrogen used to provide the inert gas can also provide the cold for condensing (see above).	Mostly for solvent-based coating systems and similar	Case- specific; maintenance frequency of process units and number of product line changes are important factors	System offered/promoted by BOC

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Condensation/recovery by temperature pressure cycle on process vent stream (Brayton cycle)	No examples found on petrochemical-type plants: mostly for solvent-based product manufacture and application		
Biofiltration : Biomass on perforated trays or similar	Odorous chemicals – Quest Ethanol, MEK, Formaldehyde (< 55mg/m3 feed) Can handle aromatics, but needs extra biomass. – Monsanto	99.9%, dependent on residence time	Moisture control is important, sophisticated systems use load cells. Minimum air content = minimum of 5% of feed flow. Load changes smoothed by use of activated carbon. Small amounts of SO_2 can be mopped up by adding lime (CaO)
Bioscrubbing Wet scrubbing plus biotreatment of liquor	Odour reduction – Dow Amine derivatives	100% (i.e. below detection limit) to 20 mg/ml	
High performance techniques: e.g. destruction by ozone/UV, destruction by corona discharge	No examples identified on petrochemical type plants	99.99%+	Usually directed at low volumes of materials of high environmental impact such as certain halogenated organics
Fugitive Emissions – leaks from flanges, pumps, valve glands, and compressor seal systems			
Release Inventories: Development of an inventory based on correlations and measurements as a basis for defining improvements	Most operators are doing this, but with varying levels of commitment		This concept is more readily applicable to plants using solvents than those where the organics are part of the process stream. A mass balance may not be accurate for petrochemical and large scale organic processes. The release inventory depends on sophisticated measurements or on standard emission figures for each type of fitting.

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Solvent management programme: as proposed by the EU; includes approximate mass balance			This concept, too is more readily applicable to plants using solvents than those where the organics are part of the process stream
Monitoring of ground concentrations, in plant and outside; to be used in methodology to calculate total emissions from the plant	Standard practice to measure many organics for occupational health reasons A network of online monitors is usual for VCM, for example		Consideration of actual ambient (outside plant) concentrations is part of the regulatory approach of many countries, including the UK BPEO methodology
Leak detection and repair programme, possibly with installed analysers	ARCO –40 000 points per year Borealis (ethylene) – Finland Fina (ethylene) – Antwerp Six-monthly check - acetylene		Many operators are doing this, but with varying levels of commitment.
Low leakage pumps: Double mechanical seal Seal-less pumps - magnetic drive or canned pump	Used where occupational health requirements specify them, carcinogens for example. Increasingly, where the volatility of the hydrocarbon is such that it would cause a significant release to the environment, or that it would be released above its flash point, then a pump with improved containment is often a requirement. Seal-less pumps are not usually mandated, though.	100% for seal-less variety	Maintenance practice also determines how well pump seals perform.
Piping design: Minimising the length of sample lines, minimisation of flanges; use of fast loop systems.	A common aspect of new plant design where organic gases or volatile liquids are handled	Up to 90% abatement	Careful design is needed to ensure that items can be removed for maintenance

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Valves: Use of improved packings, in both design and materials. Use of ball valves with tight shutoffs. Double isolations for sample points.	Programme of progressive replacement of valves, seals etc with superior containment performance – Borealis, Fina, Amoco	90%	
Intermittent Vent – including relief and blowdown requirements and process start up and shutdown			
Blowdown drums The vent is sparged through water to condense the majority of the blowdown requirement, followed by recovery from water. Further treatment of the vent gases may be necessary.	Where a good proportion of the organic can be condensed by water at 10-30°C and the separation of the hydrocarbon and water is adequate. Examples – xylenes	Depends on the organic compound	
Flare Stack: Desirable features include Nitrogen purged Stack height adequate to protect operators from radiation burns, and to provide adequate dispersion in case of flame failure. Pilot flame indication and systems to prevent the pilot being extinguished. Steam control to prevent smoky flares, including cameras (visual and infrared) Knockout pots to capture liquid. Pipework designed to prevent slug flow of two phase mixtures.	Examples: Process and Relief vents – DSM. VCM/PVC , - Borealis ethylene/polyethylene Processes gases – Norsk Hydro PO/PG/MTBE - ARCO Flame combusters, benzene loading facility – John Zinc	98% at design flare rates.	Can be designed to minimise noise. Level of control often reflects frequency of use, i.e. infra red flame detection steam control may only be suitable where the flare demand is high.
Refrigeration on vents from Pressure/Vacuum Valves for low pressure storage tanks	VOCs - Dow	95%+	Ammonia chilled loop

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Maintenance good practice including: Receipt vessels for liquids Purges to receipt vessel or to flare; minimal steaming to atmosphere	Widespread application		
Start up/Shutdown good practice including : Procedures or systems to minimise purges to relief and blowdown systems. Minimisation of inventories prior to shutdown. Procedures for dealing with purges from equipment prior to inspection at shutdowns	Widespread application		
Nitrogen Purge systems – control of nitrogen flow	Many blanketed systems		As the nitrogen will pick up VOCs, losses can be minimised by good control of the nitrogen flow, whilst still ensuring oxygen levels are below acceptable levels.
Losses of VOCs from Water Systems			
Analysis of cooling water: Monitoring for leaks from heat exchangers etc	Common practice on refineries and larger petrochemical plants		The need for this depend on the age and condition of the equipment
Degassing of cooling water and vapour treatment			A possibility if there is significant ingress into cooling water
Oil/water separation: (removal of non-water miscible organic phase, reducing further losses to air)	Usual part of site wastewater treatment		

Table 4.1 VOC abatement technique review (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Restriction of evaporation from basins such as oil/water separators by use of cover, floats etc	Common technique in refineries		
Covering basins such as oil/water separators and venting to treatment unit	Common technique in refineries		
Air stripping of organics, return to process, recovery, or fuel	e.g. stripping of EDC	90%	This measure may be a method of water treatment as well as reduction of atmospheric VOC emissions
Steam stripping of organics, return to process etc.	e.g. solvents – Dow	90%	As above

4.2.2 Combustion Gases

Many hydrocarbon processes use large packaged boilers systems or direct fired furnaces to provide heat for reactions and separations. These can be fired with natural gas, process gases (offgases) or oil. The abatement techniques reviewed in this section minimise NOx, SOx, and CO (greenhouse gases) in the flue gases of these heaters. Chemical oxidation processes also produce NOx, CO_2 and CO as by-products. Some of the identified techniques are also applicable to these processes.

Combustion processes are, of course, covered under a separate Guidance Note to that for petrochemical and large organic processes. This topic is briefly included here to address cases where the combustion device is an intrinsic part of the process plant or is otherwise not categorised as a combustion plant.

Table 4.2 lists abatement techniques discussed with operators and equipment manufacturers. Virtually all operators either had installed low NOx burners, or had considered their use but could not retrofit the burners to older furnaces because of flame impingement restrictions.

Table 4.2 Combustion gases abatement techniques

Technique	Plant/Application	Targets/ Performance	Comments
Choice of fuel: The selection of a 'clean' fuel can bring environmental benefits including reduced pollution by-products (e.g. SO_2, HCl), reduced particulates, and increased controllability. Lower C:H ratio, as in natural gas, also reduces CO_2 emissions per unit of heat.	Many petrochemical processes, the largest consumers being ethylene crackers, refineries and aromatics plants (very large throughput processes requiring high temperature reactions and separations:) Use of natural gas – Fina (Belgium)	Primarily the substantial reduction of SOx, often to meet a bubble limit equating to EU standards.	Natural gas is cleaner than oil, hydrogen is better (no CO or CO_2). Quality and composition of gas on a large integrated site is dependent on which plants are operating, and may vary. For externally purchased fuel, cleaner fuels generally command a price premium.
Burner control: Automated control system	Standard	Control of CO, NOx, particulates to national limits	
Flue gas analysis: e.g. analysis to prevent partial oxidation of carbon. and minimisation of smoky flues – Total.	Many petrochemical processes and operators e.g. Total	95%+	
NOx			
Low NOx Burners and Ultra Low NOx Burners	Many petrochemical processes Low NOx burners employed on steam cracker (ethylene furnaces) – Borealis, Amoco, Fina and on steam boilers - Borealis, EVC	Up to 70% reduction of NOx	With secondary fuel injection to suppress NOx production
Other combustion modifications: e.g. flue gas recycle, reduced preheat	Specific examples not identified		May not be feasible on existing units
Selective Non Catalytic Reduction: e.g. injection of ammonia or urea	Specific examples not identified	Around 60-80%	Requires a specified temperature window; may not be feasible

Table 4.2 Combustion gases abatement techniques (Cont.)

Technique	Plant/Application	Targets/ Performance	Comments
Selective Catalytic Reduction (SCR): Catalytic reaction with ammonia	Specific examples not identified	Up to 95% with LNBs	German producers report a request to use SCR on a new ethylene plant (steam cracker) but examples of actual installation were not identified.
Oxygen enrichment: Minimise or eliminate nitrogen oxides by replacing air with oxygen	Chemical oxidation processes using air as an oxygen source.		
SO_2			
In-furnace injection of alkali	Specific examples not identified	Around 40%	Unlikely to be feasible in process equipment
Flue gas treatment e.g. Semi-dry, limestone-gypsum, Wellman-Lord; once through caustic scrubber	Specific examples not identified	Up to around 95%	Costly; likely to be on central boiler plant (Combustion Plant) if anywhere
Particulates			
Bag filter	Specific examples not identified	99%	
Electrostatic Precipitator	Specific examples not identified	99%	

4.2.3 Other atmospheric emissions

Volatile organic compounds and combustion emissions are those most characteristic of petrochemical and large scale organic facilities. Other possible emissions include carbon monoxide (as part of the process tail gas), soluble inorganic gases, and particulates, both of product solids such as from driers and heavy metals, perhaps from catalyst regeneration. Some techniques are reviewed on Table 4.3.

Table 4.3 Abatement techniques: other emissions

Technique	Plant/Application	Targets/ Performance	Comments
Particulates			
Hoods ducts and blowers to collect dust		99%+	In 'dry-side' applications such as polymer handling
Cyclone	Many petrochemical processes e.g. cyclones applied to combustion gases from decoking operations of ethylene furnaces e.g. cyclones on drier vents	85%+	Usually multistage
Bag filter	Commonly employed, though they may also be installed to protect process equipment rather than the environment. Filters are used on polymer (polyethylene)plants such that dust does not present any major hazard. Recovery and recycle of particulates	95%+	
Electrostatic precipitator		99%+	
Wet scrubber e.g. spray		90%+	
Soluble inorganic gases (e.g. acid gases, ammonia)			
Wet scrubber	Standard for this application	90% +	
Carbon monoxide			
Tail gas incinerator	e.g. on phthalic anhydride		
Zeolite Adsorption: Pressure Swing Adsorption/	CO from CO_2 - Bayer	95-99%	
Nitrous oxide			
Catalytic reduction	Adipic acid production e.g. BASF		
Incineration: reducing atmosphere	Adipic acid production e.g. Du Pont		

4.2.4 Wastewater

Wastewater arises from several sources, which may be broadly split into those arising from the process and stormwater in areas where there is some risk of contamination, perhaps from spills of hydrocarbons or other process streams. The wastewater from the process may be continuous, such as when an aqueous phase is separated from the organic process steam, or intermittent such as water or steam condensate from tank cleanout. Of course, the production of aqueous effluents is minimised on modern plant where feasible by avoiding direct contact between, for example, cooling water and the process streams.

Many operators, particularly those on sites with a number of processes, have integrated schemes for dealing with water pollutants, comprising of primary separation techniques, pH control and biological treatment. When water recycling occurs, it is often at a site level, with treated wastewater acting as cooling water make-up, for example. The following review is focused on treatment techniques that are of wide applicability.

A wide range of treatment processes was discussed with operators, from the types of biological treatment or physical separations used, to policies for drainage systems. Table 4.4 summarises these techniques.

Table 4.4 Wastewater treatment techniques

Technique	Plants/Applications	Targets/ Performance	Comments
Oily phase			
Phase Separation: e.g. Settling basin	Separation of free organics from a two phase system – a widely applied technique	90%	Recovery of oil should be effected as early as possible in the process, to avoid additional transfer of the organic to the aqueous phase.
Oil/water separators	DSM, Total	Limited by the solubility of the organic compound in water typically 10 – 2000 ppm at ambient temperatures.	Oil can be recovered to the process. Mass flows of effluents can be measured using weirs or on-line meters such as ultrasonic flowmeters. Together with samplers, this can provide mass flow estimates. Provides a large residence time to minimise the impact of losses of containment.
Decanters	Primary separation of oil/water mixtures.	90%+	Decanters rely on good control of the interface between the oil and water phases. The water phase will typically have a high degree of saturation and may need further treatment.

Table 4.4 Wastewater treatment techniques (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Hydrocyclones		95%+	
Chemically enhanced settling: Emulsion breaking etc	Applicable mostly to refineries		
Membranes	Ultrafiltration of waste oil to remove water prior to external disposal - Dow	95%+	Membranes can be used to further purify the recovered hydrocarbons. This can be very cost effective if the waste oil is disposed externally.
Suspended Solids			
Settling basin/lagoon	Common technique		For large volumes, particularly if settled solids can stay as floor
Screens of various types	Common technique	85% - depends on particle size and shape	For tramp material and coarse particles
Filter Beds e.g. large beds of solids in lagoon or similar e.g. filter bed of sand in vessel; backwashed periodically	More common on inorganic than organic plants	95% -depends on particle size and shape	For fine particles
Flocculation and settling in clarifier	Standard technique for several contaminants	e.g. 90%	
pH			
Neutralisation Many process effluents need neutralisation prior to discharge or secondary treatment.	Common technique e.g. amine derivatives	Performance depends on the control system to cope with changes to the feed composition.	A better response profile and hence better control of pH is claimed for some reagents. An example of this is injection of CO_2 to neutralise alkali streams.- BOC Products of neutralisation may precipitate e.g. with sulphuric acid and lime

Table 4.4 Wastewater treatment techniques (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Dissolved salts			
Dilution	Common technique		Not a recommended technique, but often occurs as a consequence of common site treatment systems
Flocculation and settling	Common technique	Variable	Often a significant reduction in dissolved salt loading in site system
Chemical precipitation	Examples not identified on petrochemical and organic plants		Can involve substitution of ions in effluent rather than removal
Evaporation	Chloride salts – 5m^3/h and >100 000ppm feed conc. – Bayer	Reduced to 3000ppm COD – 97% reduction of chloride to bio-treatment.	Evaporation, condensed evaporate to a biological unit and concentrated salts to a special incineration unit Bayer
Crystallisation and recovery of dissolved solids	Organic Acids, e.g. terephthalic acid Dissolved inorganics e.g. sodium sulphate from cellophane production	Dependent on solubility and inlet concentration	
Concentration e.g. by membrane units	Examples not identified on petrochemical and organic plants	High reductions in effluent (90%+) feasible	Concentrated liquors pass to suitable disposal
Ion exchange	Examples not identified on petrochemical and organic plants		Used for example on some on fertiliser plants to recover nitrates

Table 4.4 Wastewater treatment techniques (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Organics/Oxygen Demand			
Aeration e.g. in lagoons	Common on older sites	70%+	
Aerobic biotreatment e.g. conventional activated sludge system Direct oxygen injection -BOC, Air Products - is used to intensify aerobic biotreatment processes. This process can also reduce the volume of biomass purge. This can be an economic way of increasing capacity or coping with surges. The Deep shaft process is another method for enhancing the metabolic process involved in biodegrading, in this case by using a large head of liquid (100m) to increase pressure and hence oxygen mass transfer rates. Closed systems: e.g. Bayer Tower Biology uses a closed tank with injectors to improve mass transfer to the sludge, reducing offgas. A closed system can also minimise odours.	Simple or degradable organic molecules: common technique used by, e.g. DSM, Bayer, BASF, Norsk Hydro, Quest, Total, Borealis, EVC, Fina, Amoco	Around 90% over total system. Effectiveness is a function of the biodegradability of the feed, residence time of the system and oxygen supply.	Usually copes with a range of process waste streams and is part of an integrated system for effluent treatment. Can be difficult to operate systems with variable feed quantity or quality without good control and buffering systems
Anaerobic treatment		90%+	For more concentrated wastes
Chemical flocculation	Non biodegradable organics from ethylene/polyethylene plants. Solid sludge is concentrated, dried/filtered prior to landfill e.g. Amoco - Belgium		

Table 4.4 Wastewater treatment techniques (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Solvent extraction	Used on cokeries to extract phenol from liquor; no examples identified for petrochemical and large organic plants		Appropriate for specific pollutant at the process, not site treatment system
Adsorption: powdered carbon in effluent	Established technique; used on nitrobenzene wastewater	95-99%	
Adsorption: fixed carbon bed	Established technique; no examples in petrochemicals or large organics identified	95-99%	
Stripping of organics by air or steam with recycling, recovery or proper disposal			
Thermal incineration	For relatively high levels of organics or organics that are difficult to degrade e.g. nitrobenzene liquors - ICI	98%	More common on fine chemical production; costly in fuel input
Wet Air Oxidation Lower temperature than thermal oxidation, can be autothermal apart from startup. Loprox process licensed by BOC in the UK and developed by Bayer uses an acidified feed to reduce the operating conditions (pressure and temperature) at the expense of higher grade materials of construction (glass lined or titanium)	Treatment of toxic or chemicals or those with low biodegradability in anaerobic or aerobic biological systems Examples – long chain aliphatics, chlorohydrocarbons, larger or more complex hydrocarbons. Salicylic acid wastes – Bayer	Typically would be used as a pretreatment (60-85% reduction of COD) to provide degradable molecules for a secondary biotreatment process.	
Supercritical water oxidation High efficiency 'incineration' at supercritical conditions	Demonstration plants include ethylene plant in USA	99.9%+	Not widely used but demonstrated on commercial scale; several technology holders

Table 4.4 Wastewater treatment techniques (Cont.)

Technique	Plants/Applications	Targets/ Performance	Comments
Ozone injection, hydrogen peroxide Can be enhanced with UV light	Difficult to treat hydrocarbons, dyes, odorous chemicals. Hydrocarbons containing double bonds.	Elimination of the compound	Usually reserved for environmentally sensitive chemicals that are difficult to degrade. Ozone is efficient in breaking down double bonds.

4.2.5 Groundwater Protection

Ground protection was specifically mentioned by a number of operators. Protection methods ranged from use of above ground, pumped drains to biotreatment of groundwater. Many of the decisions for the types of techniques used to protect or remediate groundwater depend on the site history, local hydrogeology, and age.

The topic of waste disposal is included in this section as the unsatisfactory landfill or other disposal techniques could threaten soil and groundwater quality. In the context of petrochemical and large organic plants, the emphasis is on on-site disposal or treatment facilities.

Table 4.5 Groundwater protection techniques

Technique	Plants/Applications	Targets/ Performance	Comments
Paved process plant and stormwater areas draining to separation/treatment	Standard practice		Process plant paving in particular should be impermeable to process liquors
Paved loading/unloading areas draining to separation/treatment	Widespread practice		Should be impermeable to the material being transferred
Fire water runoff: drainage systems to capture run off from fire water.	Widespread practice		
Above ground drains	e.g. VCM – Norsk Hydro		Enables easy leak detection and maintenance of wastewater pipework; also preferred to reduce explosion risks

Table 4.5 Groundwater protection techniques (Cont.)

Technique	**Plants/Applications**	**Targets/ Performance**	**Comments**
Impermeable tank bunding:	Tank farms with petroleum or other organic products		
Clay lined or paved bunded areas.	e.g. clay lined bunds		Clay lining not now acceptable as new plant standard
	Coated concrete or polymer membrane examples not identified		
Tank leak detection	Specific examples not identified		
e.g. channels between tank and plinth	(but used in some refineries)		
Double walled storage tanks (above ground)	Specific examples not identified (but used in some refineries)		
Underground tank containment	Double sealed containers with leak detection systems standard on many plants		Alternative of single shell plus custom coating system in some countries
Pump out facilities from bunds:	Many plants e.g. Dow		
Systems for prevention of leaks from bunds via bund drains (locked valves, no valves)			
Groundwater monitor wells	Site-specific applications; often around landfills		Only where there is environmental sensitivity or reason to suspect leaks
Recovery and treatment of groundwater	Site-specific applications e.g. VCM/PVC – Norsk Hydro e.g. Total		Pump groundwater from wells to a treatment facility (this may fall into the category of remediation rather than abatement, but it can also be a means of containment)
Groundwater hydraulic management:	Site-specific applications; used in a number of refinery sites in Europe		Used to prevent spread of , usually, petroleum products floating on groundwater
Creation of hydraulic gradient to contain surface layer of pollution			

Table 4.5 Groundwater protection techniques (Cont.)

Technique	**Plants/Applications**	**Targets/ Performance**	**Comments**
Landwastes			
Volume reduction by dewatering	Widespread practice; usually on site wastewater treatment sludges		
Burning of organic sidestreams as site fuel	Widespread practice	98%+	Regulatory restrictions may limit the possibilities (e.g. if classified as waste incineration)
On-site incineration of organic liquids, tars, sludges	Case-specific e.g. chlorinated residues from EDC/VCM production; sludges and cokes with dioxins - several plants	99.99% DRE	Several of the big West European sites have common incinerators serving the whole complex e.g. Ludwigshafen
	e.g. nitrobenzene wastes - ICI		Economics are a major determinant in choosing on-site rather than merchant incineration; site integration and reduction in waste movements are others.
Recycling of waste streams	Highly case-specific e.g. olefin purge from polyolefin plant fed back to cracker		
Landfill design and management: impermeable clay lining or membrane, leachate management etc.	Widespread practice		Site landfills often serve several processes

4.2.6 Other techniques and good practice

Techniques mentioned by operators that contribute to reduced emissions did not necessarily fall into one of the classifications above. These tended to be good practice or systems of work. The following paragraphs capture some of these key items, which underpin good environmental performance:

a) *Written environmental procedures*

Procedures should cover key plant operations which affect the environment, including plant start up and shutdown, and key controls on emissions. They should be readily accessible and should be controlled documents.

b) *Written design standards and procedures covering prevention of losses of containment*

These should state policy on design standards for new equipment and plant. Documented procedures for prevention of losses of containment during maintenance as well as policy for vessel and pipework isolation standards should also be included.

c) *Training of operating staff*

All operating staff should be trained to a level that they can carry out their job responsibly with respect to IPC. This should include awareness of the impact of the chemicals processed, where emissions occur from the process, and how to minimise them. Training should clearly state what is required to comply with the IPC authorisation. Records should be kept of training given.

d) *Key instrument calibration*

All of the process instrumentation key to minimisation of losses to the environment should be calibrated to a written and approved methodology and frequency. Again, this system should be auditable.

e) *Good alarm/measurement and control systems*

Use of appropriate alarms and controls should minimise process losses to the environment. Instrumentation systems need careful consideration not only to providing the correct measurement or alarm, but also giving the information to the operator in a way that can be acted upon in a suitable time frame. For example too much information can slow down a response to a situation or an alarm that is set at an inappropriate level can cause “operator fatigue”, potentially resulting in the alarm being ignored.

f) *Commitment to operating excellence and high standards*

Without this as one of the core values of the company, an ethos of ensuring production rather than truly minimising emissions may prevail.

g) *Good incident review and reporting systems*

Events such as near misses, actual losses of containment should always reviewed, and recommendation reached and implemented. A formal procedure requiring managers to complete a review of incidents ensures this happens to an agreed timescale, and the recommendations are disseminated properly, and acted upon.

h) *Clear environmental responsibilities*

Everyone involved in operating an IPC authorised processes should know exactly what their responsibilities are to maintain compliance with the authorisation.

i) Energy/material efficiency programmes

Much of the public domain solutions to environmental abatement concern end of pipe treatments. Process development concentrating on improving energy integration and material recovery and recycle can provide far bigger improvements. Good plant management teams will have a commitment to examine these process improvements. Further, design standards on process integration, intensification etc will ensure new process designs consider environmental impact at an early stage. These techniques may be reviewed formally in the development of a project.

j) Auditable systems

Auditing is an important part of any IPC authorisation. Internal company audits are a way of maintaining focus on compliance with IPC. Auditing will ensure that actions are recorded. For example, results of analysis, instrument calibration routines, and training.

k) Awareness/measurement of environmental performance and compliance

Displaying, reporting and discussing emissions, incidents, compliance is essential to motivate teams to continue to minimise and prevent emissions.

4.3 Review of selected techniques

4.3.1 General

In this part of the report, a number of techniques are reviewed in greater detail. The techniques selected are those which are relevant to a large number of the processes studied.

The review is intended to compile information of practical use to Inspectors in determining BATNEEC and BPEO. This focuses in particular on:

- technical applicability
- economics
- environmental performance.

Economics are calculated in a simplified way for most of the techniques. This means that additional operating labour and allocated overheads are omitted from the calculation, recognising the incremental nature of the abatement technique. In a few cases, the abatement technique does require more operators and this is then taken into account. The elements of costs of abatement are summarised in Table 4.6. Where a credit is given for useful material retained within the process, this is costed at (very approximately) cash cost of production rather than delivered market price.

Table 4.6 Elements of costs of abatement

	Most Cases	*Special Cases*
Variable costs		
Materials consumed	✓	✓
Fuel and other utilities	✓	✓
Saving (credit for product not emitted)	✓	✓
Fixed costs		
Operating labour		✓
Maintenance	✓	✓
Rates, insurance	✓	✓
Overheads		✓
Capital charge		
Annualised charge	✓	✓
Capital costs		
Equipment, fittings (IBL)	✓	✓
Offsites (OBL)	As appropriate	As appropriate

Notes: IBL = Inside Battery Limits
OBL = Outside Battery Limits

Unit costs are typical UK costs in 1997. Unless known otherwise, default assumptions are that maintenance is three percent of IBL capital cost per year (labour and materials) and that rates and taxes are one percent of total capital cost.

The capital charge is the annualised cost of capital, calculated using a discount rate of 10 percent (real) and a lifetime of 10 years. This is equivalent to approximately 16.25 percent of capital cost per year. The same basis was used in a DTI-commissioned study on the reduction of VOC emissions (Costs and Benefits of the Reduction of VOC emissions, May 1996, ERM Economics and Chem Systems Ltd). It should be noted that this capital charge relates more to typical costs of capital than to the hurdle rate that companies would apply to investments made for economic reasons. As the capital charge is a significant part of abatement costs in many cases, this factor is important.

All costs are indicative, and actual details will vary from site to site. This applies in particular to retrofits, where characteristics of the layout and supporting structure may vary widely. For some techniques, it is difficult to identify the incremental cost.

The analysis relates to the cost of abating a particular pollution source. In Section 6, the pollution control costs are put in the context of the economics of relevant production operations.

4.3.2 Costs of VOC abatement

The requirements to apply BATNEEC and to satisfy BPEO criteria do not necessarily suggest a defined cost per ton abated as a cut point. However, some Inspectors have suggested that information on typical costs per ton abated would be useful to place specific applications into context.

A summary is therefore given in Table 4.7 of selected data from the DTI-commissioned study mentioned above.

Table 4.7: Cost of VOC abatement [1] *(£ per ton)*

	Average cost	Marginal cost
Chemical industry	682	10 090
All sectors studied	660	10 090

1) Costs and Benefits of the Reduction of VOC Emissions from Industry, 1996

The data in Table 4.7 are approximate estimates of costs relating to likely implementation of IPC requirements. A reduction of VOC emissions (from a 1988 base) of around 60 percent from the chemical industry is implied. The marginal cost per ton of abatement relates to installation of a vapour recovery unit on loading facilities on a medium-sized chemical plant.

The information is presented only as very broad background. The circumstances of individual plants will affect the decisions of Inspectors. It should also be noted that a high cost per ton of VOC abated might be justified for VOCs with particularly high environmental impact.

- All VCM in the slurry leaving the recovery vessel will leave the plant directly to the environment or in the PVC product. It is difficult to drive off the VCM in the PVC product using a drier. Removal of the VCM from the drier vent gas is also difficult. The emphasis is therefore on removing VCM adequately in a steam stripper. In the emulsion PVC process, the latex may be stripped in the reactor batchwise or in a separate vessel either batchwise or continuously.

- Fugitive emissions are controlled with high integrity equipment and fittings as on the EDC/VCM process.

- PVC dust from the driers is another atmospheric emission associated with these plants. Some plants use cyclones for dedusting the dryer vent. Installation of fabric filters is effective and relatively inexpensive.

Aqueous Effluents

- Water used in the reaction is separated from the PVC slurry after stripping. Other sources include steam condensate, washwater and seal water. This water typically contains several parts per million of VCM. A steam or air stripper is often used to reduce the chlorinated organics in the aqueous effluent. The stripped material may be sent for incineration or other treatment. The VCM in the water can be reduced to under 1 mg/litre. It is arguable that a higher limit should apply to stand-alone emulsion PVC plants, because fine particles in the effluent tend to block stripping equipment.

- PVC in the wastewater can be removed by conventional wastewater treatment.

Landwastes

Off-specification product and other solids are usually sent to appropriate landfill. Wastewater treatment sludge may be incinerated. Solids from emulsion PVC plants may contain VCM at over 1 000 mg VCM per kg PVC. This needs to be stripped or disposed of as hazardous waste, preferably incinerated to avoid VCM loss to atmosphere.

c) International legislation

EC Directive 90/415/EEC covers the manufacture and use of 1,2 dichloroethane (DCE) and is relevant to releases to water from the production of vinyl chloride monomer (VCM). In this report, DCE is termed EDC, or ethylene dichloride, which is the more usual industry designation.

Description: Vapour recovery or destruction

Floating roofs and balance lines are methods of reducing emissions, particularly on loading/unloading. If the size of a tank makes it uneconomic to fit a floating roof, or if a sealed vapour balance line is not feasible, vapour recovery or destruction techniques can be applied.

These techniques are described in general in subsequent sub-sections such as Section 4.3.3 to 4.3.5. When applied to tanks and transfer systems, the following notes apply.

Vapour recovery systems are available in several forms, including:

- **Liquid absorption**

  The VOC can be absorbed into a heavier organic stream, usually at around 95 to 98 percent efficiency. One option is to recover the absorbed VOC in an absorber system. This is used in the Cool Sorption system on gasoline, for example. The gasoline is absorbed in and stripped from kerosene. An outlet concentration of 35g/m^3 is typical. The other possibility is to use the loaded absorbent as fuel. The choice will be dictated by technical characteristics and economics. Water-soluble organics can be removed in a scrubber. Stripping or rapid water treatment is necessary to avoid aqueous pollution.

- **Carbon adsorption**

  Carbon adsorption in this application has the attraction of being able to act as a buffer for fluctuating pollutant load, such as on loading. The possible disadvantages are that the organic load may be high, requiring a large bed, and the risk of explosion needs careful management. Removal efficiencies of 98 percent are achievable.

  As with absorption, the VOC can be recovered or, if the loading is very light, the carbon can be sent to disposal with the organic. Vacuum regeneration of carbon is known to be used on certain gasoline applications in Europe.

- **Other recovery techniques**

  Other recovery techniques include condensation with a combination of chilling and compression, and membrane systems. One producer referred to the use of membrane units to control benzene in particular.

One-stage vapour recovery, while removing most of the emission, is unlikely to meet current emission concentration guidelines at peak load. Two-stage systems are known to be used on, for example, gasoline and solvent storage installations. Chem Systems has not identified cases of use on petrochemicals or large scale organics, but this does not reflect any technical problem. Two-stage systems may use liquid absorption, followed by carbon adsorption. This reduces the load on the absorber and can reduce the gas entering the adsorber to below its explosive limit.

Two-stage systems can certainly achieve the TA Luft limit of 0.15g/m^3 for gasoline.

On gasoline systems, a large part of the capital cost is in loading gantry modifications. It may be most economic to install devices on each tank or loading bay, as appropriate, rather than to manifold everything to a single recovery unit.

Vapour destruction by oxidation is a possibility, but gas flows on loading and unloading will be intermittent so that control may be difficult. This problem may be avoided if the tank/transfer vents join a larger continuous system passing to an incinerator or boiler.

With any vapour treatment system, the volume of gas is important in determining size and economics. The air flow may be dictated by the need to avoid explosive conditions. In this case it may be possible to reduce the gas flow substantially by using an inert gas system.

Economics

Indicative economics for control of VOC losses in storage and transfer are shown on Table 4.8. The hypothetical case is based on a liquid with a vapour pressure of 40 kPa, storage in two tanks of 5 000m^3 each, and transfer of 100 000 tons per year. For the vapour recovery unit (VRU), a single unit is assumed. Four road tankers are also included in the scope.

Cost data have been broadly estimated from vendor data and published information, largely on refinery installations. A nominal credit of £150 per ton has been given for 'saved' VOC.

Table 4.8 Cost of VOC containment: storage and transfer

Abatement technique	Capital cost *(£000)*	Operating cost *(£000)*	Annualised cost *(£000)*	Cost per ton VOC *(£/ton)*
External floating roof: secondary seal	28	-400	4 140	650
Internal floating roof	79	-355	12 300	965
Road tanker mods	80	-1 300	11 700	835
Single stage VRU	710	22 425	137 650	2 900
Plus second stage VRU[1)]	115	4 240	22 700	9 550

[1)] Incremental

The capital cost of the vapour recovery units (VRUs) is high. It corresponds to a liquid absorption/desorption system with gantry modifications and, for the second stage, a carbon adsorption system with vacuum regeneration. Costs could be lower in specific circumstances, such as if the absorbant and adsorbant are sent for fuel use, integration with the process, or disposal, rather than requiring dedicated regeneration.

The cost per ton of VOC abated will, as a first approximation, vary inversely with vapour pressure.

Environmental performance

The environmental performance of floating roofs depends largely on the accuracy of fabrication and is difficult to measure. These are no obvious environmental trade-offs, although appropriate design features are needed with external roofs, for example, to prevent rainwater ingress. Similar considerations apply to modifications to road tankers.

For vapour recovery units, the system can be designed to achieve specific recovery efficiencies or emission concentrations.

4.3.4 Incineration of gaseous VOC emissions

The destruction of organic compounds by incineration is a well established technology. Economic cost is often a point of prime concern with operators as the costs of supplementary fuel can be significant. Other important issues are the destruction efficiencies for specific chemicals of environmental concern, and the formation of by-products.

Two main categories of incineration are described below: thermal (high temperature) incineration and catalytic incineration.

Description: thermal incineration

Organic chemicals are destroyed by thermal incineration at high efficiencies, typically well over 98 percent. It may be difficult to achieve specific emission limits of, for example, 20mg/m^3 if the inlet organic concentration is high – 15g/m^3 for example. Destruction efficiencies of up to 99.5 percent are quoted for regenerative oxidisers, however.

The necessary incineration conditions depend upon the organic species and may also be regulated by law or industrial standards. A temperature of 600-650 °C is usually the minimum, with a residence time of at least 0.3 seconds. Temperatures of 800-850 °C with a residence time of at least one second are more usual. For chlorinated organics, a temperature of at least 1200 °C with six percent free oxygen, and a residence time of two seconds are required.

The main technical limits of the thermal incinerator are summarised below.

- The potential for incomplete combustion is of particular concern for halogenated organics, when there is a possibility of formation of dioxins and furans. In practice, with the combustion conditions described above and good distribution characteristics, the formation of these toxic materials can be minimised. However, in hazardous waste and solid waste incinerators, it is now common practice in several European countries to install activated carbon beds, or to inject carbon, to adsorb any contaminants from the tail gas. Even where an incinerator is part of a chemical process rather than being classified as a waste incinerator, inspectors will possibly wish to apply a limit of 0.1ng/m^3 (TEQ) on dioxins and furans.

- Oxidation of a hydrocarbon or oxygenate produces carbon dioxide, carbon monoxide and water. With other elements in the molecule, combustion products may cause technical or environmental difficulties. Acid gases such as SO_2 or HCl might require removal from the flue gases to meet emission limits, for example, and necessitate careful design to avoid corrosive conditions.

- In practical terms, there is a minimum capacity for thermal incinerators. Combustion chambers typically start at around one cubic metre. At very low flow rates, the unit would be uneconomic in addition to possible gas distribution problems. With a residence time of two seconds and a combustion temperature of 850 °C, one cubic metre is equivalent to a waste gas flow at ambient conditions of roughly 400-500 m^3/h, if no fuel or dilution air are needed.

- Incinerators are appropriate for continuous flows. Occasional releases are often more appropriately handled by flares.

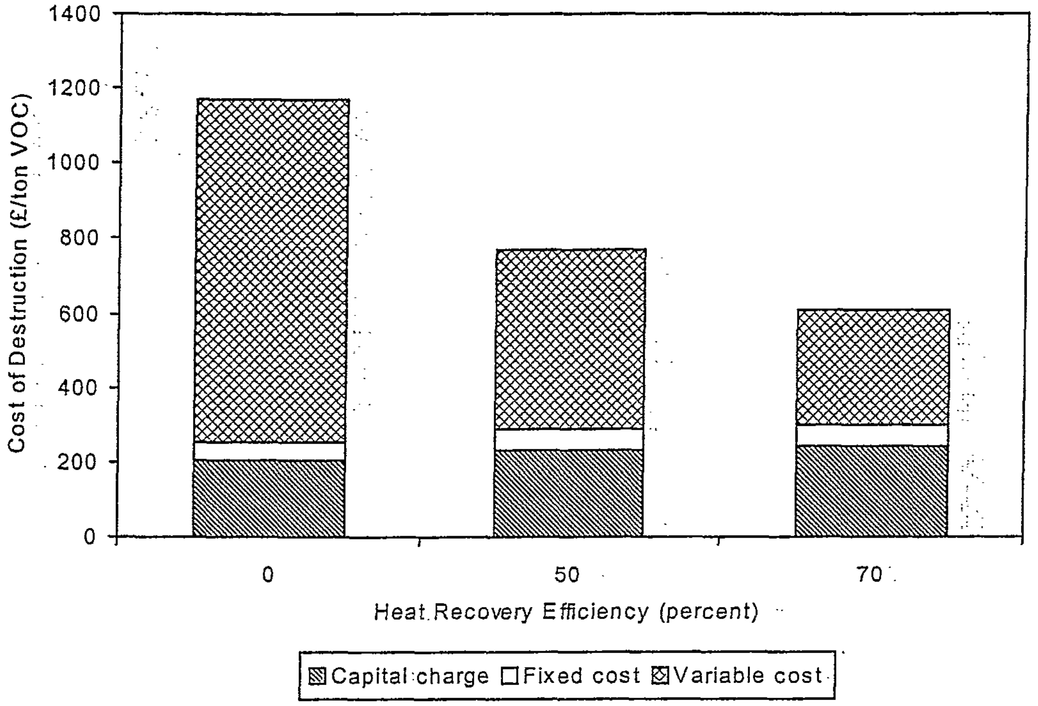
The greatest disadvantage of thermal incineration is the cost. At typical concentrations of VOCs, supplementary fuel is needed to achieve the required combustion temperature. Figure 4.1 shows the cost of destruction of a typical waste gas, 25 000 m^3/h air with 5 g/m^3 of ethyl acetate, at different energy recovery efficiencies. While the capital cost typically increases with higher efficiencies, this is far outweighed by the cost of fuel. For this reason, incinerator manufacturers have focused development on high efficiency designs.

Basic approaches are shown on Figure 4.2. Heat can be recovered from the hot flue gas, either to preheat incoming waste gas or dilution air, or to raise steam. Energy recovery efficiencies of 50-70 percent are typical for these recuperative systems. With the regenerative design, the hot gases heat a sink material such as gravel or ceramic packing and, in doing so, are themselves cooled. The heat is recovered by either reversing the gas flow across the bed or by a duplex system. With regenerative designs, heat recovery efficiencies of up to 98 percent are claimed.

Two further variants should be noted.

- The economics of incineration are very dependent on the concentration of organics in the gas stream as noted below. One option is to pre-concentrate the stream prior to incineration. This is most commonly effected by an adsorption-desorption device, and is described under adsorption below (Section 4.3.5).

- Combustion of the organics in a site boiler or fired process heater may be feasible. If the stream that contains the organics can substitute part of the combustion air, or secondary air, the economic problem of incinerating a dilute stream is avoided. However, the technical conditions for efficient destruction must be met.



Basis: 25 000 m³/h, c. 40kJ/m³

Figure 4.1 Cost of thermal oxidation at different energy recovery efficiencies

Description: catalytic incineration

Oxidation of organics can be effected at considerably lower temperatures than for thermal incineration by using a catalyst. Oxidation temperatures of 320-450 °C are typical. The lower temperatures mean a substantial reduction in fuel requirements and a smaller combustion chamber volume, both decreasing the cost. There is an upper temperature limit for catalyst effectiveness, usually of around 550 °C, although for special catalysts the limit can be up to 750 °C. The temperature limit means that dilution air can be required at high VOC loadings.

Catalysts fall into two main groups. Metal oxide catalysts are based on metals such as copper, manganese and chromium. The other group is precious metal catalysts, usually platinum and palladium. Precious metal catalysts are usually supported on a substrate such as aluminium or expanded metal.

In technical literature, destruction efficiencies of around 95 percent are quoted. Case studies supplied by vendors can, however, show efficiencies comparable to those of thermal incineration, at 98-99 percent. The destruction efficiency depends upon, amongst other things, the ratio of the catalyst bed volume to be waste gas flow. This has implications on the capital cost.

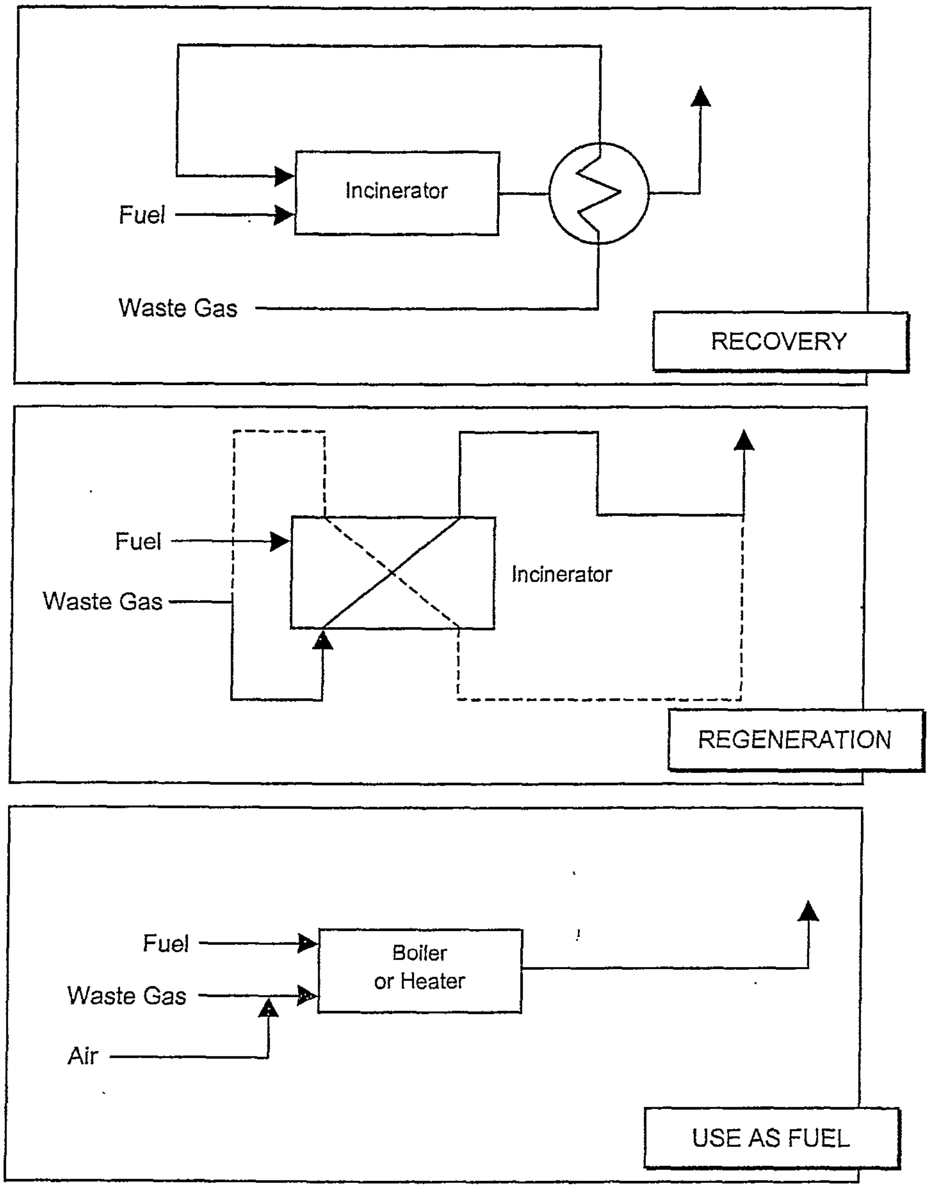


Figure 4.2 **Energy recovery: thermal oxidation**

Probably the greatest limitation of catalytic incinerators is their vulnerability to contaminants. There are a number of potential contaminant problems, as outlined by the catalyst supplier UOP.

- Inorganic solids such as dust and rust can deactivate the catalyst. An upstream filter is a preventative measure, while a contaminated catalyst can be washed or cleaned by air blowing.

- Heavy hydrocarbons can deposit a tarry layer on the surface of the catalyst. Increased inlet temperatures can help in avoiding deposition, while a contaminated catalyst can be regenerated by burning of the tar at 500 °C.

- Halogen and sulphur compounds cause temporary catalyst deactivation. For this reason, fuel oils containing sulphur (or heavy metals) should not be used as supplementary fuels. Increased inlet temperatures reduce the deactivation and, in addition, some halogen-resistant catalysts are also available.
- Some catalyst poisons convert to a solid inorganic coating in the catalytic combustion process and permanently deactivate the catalyst. These poisons include compounds of organic silicones, metals and phosphorus. One option is to use pre-treatment beds to adsorb the contaminants. The loaded adsorbent material would need periodic disposal, typically to special waste landfill. Chemical cleaning of a contaminated catalyst by the catalyst supplier can be possible, but this is feasible for a limited number of regenerations as the life is shortened each time.

Economics

Generalised economic models for destruction of VOCs by thermal incineration have been developed from a combination of public domain sources and data provided by equipment suppliers and industry analysts. The data are illustrative only and are calculated on as basis of ethyl acetate in relatively dry air. Ethyl acetate is in the middle of the range of calorific values of organic compounds. The hydrocarbons such as toluene have a higher calorific value and so require correspondingly less fuel. Other compounds, such as chlorinated hydrocarbons, have a lower calorific value.

For incinerators treating 25 000m ^{3} per hour of gas, with 2 g/m^3 of VOC in the inlet gas, the economics are summarised in Table 4.9.

TABLE 4.9 Cost of incineration for a typical gas stream

Incinerator type	Thermal recovery	Capital cost *(£000)*	Operating cost *(£000)*	Annualised cost *(£000)*	Cost per ton VOC *(£/ton)*
Thermal: no recovery	0	490	380	456	1170
Thermal with recuperation	70%	580	145	238	610
Thermal regenerative	94%	720	60	176	450
Catalytic	70%	630	98	201	510

Note 1) Volume 25 000 m^3/hr
Organics around 40kJ/m^3

The costs of incineration are sensitive to the organic loading and to the gas flow rate. Figures 4.3 and 4.4 illustrate annual costs, including capital charge, and cost per ton of VOC destroyed for the thermal incinerator with energy recovery and for the catalytic incinerator. The figures show that incineration, as expected, is costly at low organics loadings and low gas flows. The costs would be higher if, in the thermal incineration case, a higher incineration temperature than 800°C is required because of the nature of the organic compounds.

In all cases, the costs quoted exclude any pre-treatment of the gas stream.

Environmental performance

The main environmental impacts from incineration arise from the emission to the atmosphere of products of complete or partial combustion. This applies to combustion of both the organic pollutant and any supplementary fuel, taken here to be natural gas.

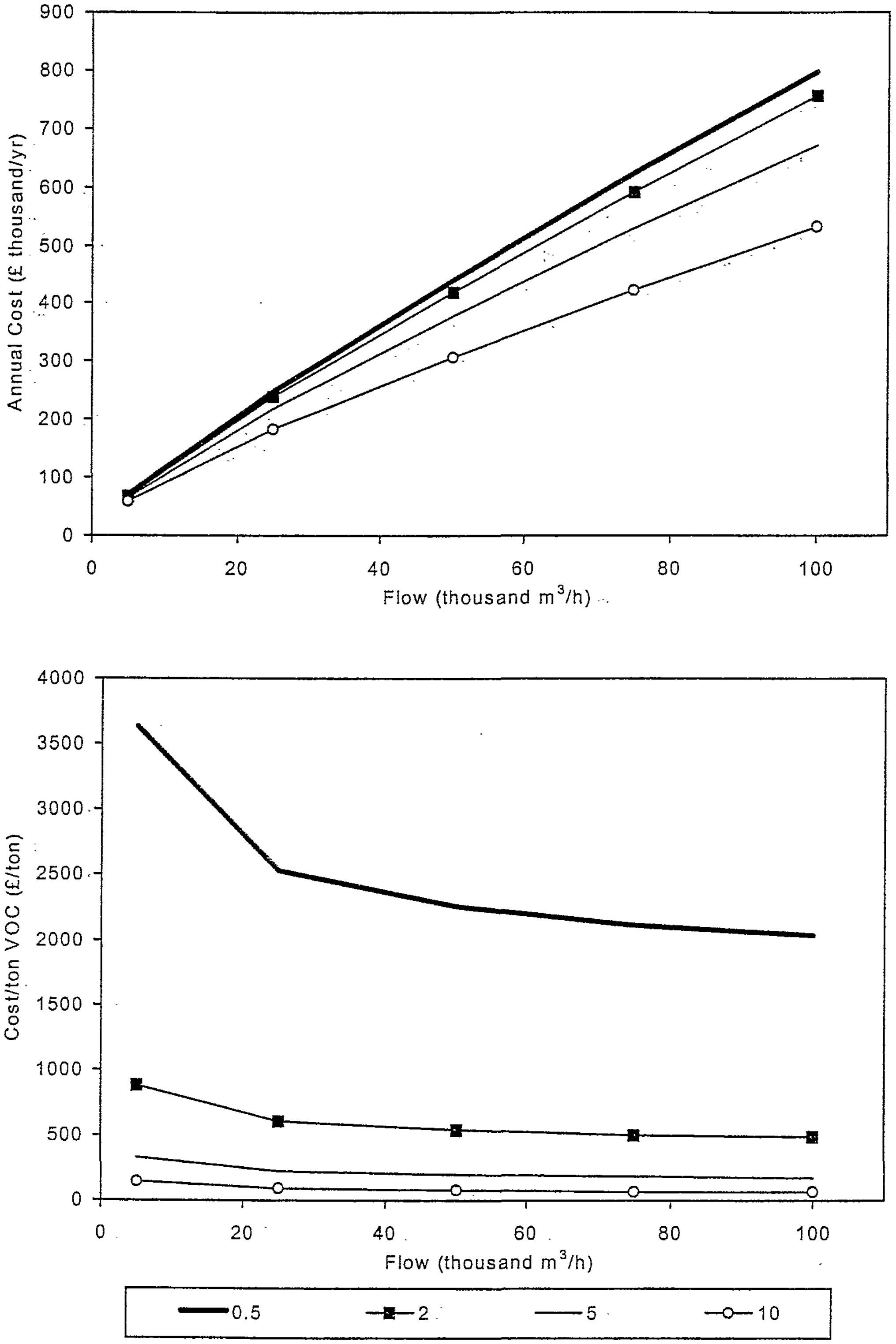
Emissions from combustion include carbon dioxide, carbon monoxide, NOx and unburnt organics. Carbon dioxide is largely unavoidable, but the use of natural gas as supplementary fuel introduces less carbon per heat unit than liquid fuels. Reported levels of CO and NOx can both be around 100mg/m^3, but this is subject to detailed design.

The combustion efficiency for organics will be 95 percent or greater. Figures of 99.5 percent are quoted for swing bed regenerative systems aimed at solvent-laden air. Higher destruction and removal efficiencies are technically feasible, given the right temperature and residence time conditions, but at significant cost penalties.

Impurities of sulphur or chlorine in the organics, or in the supplementary fuel, will be converted largely to acid gases: $S0_2$ and HCl. This may be beneficial, if small quantities of H_2S are oxidised, for example. However, if impurities are present in significant quantities, there might be a need for tail gas scrubbing.

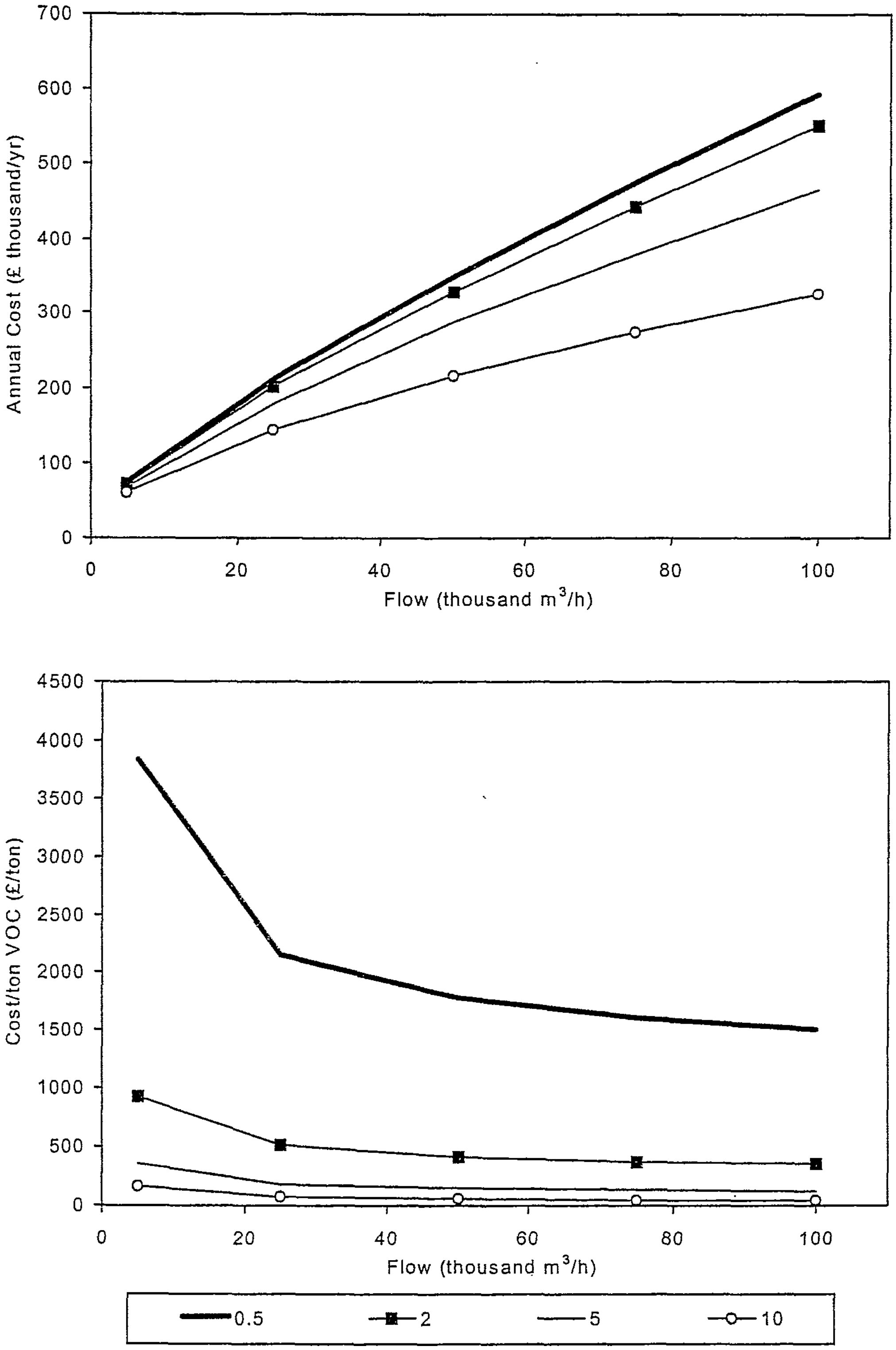
Chlorinated (or other halogenated) organics are of particular concern because of the fears of the production of dioxins and furans. Catalytic incinerators have been demonstrated on halogenated organics streams in recent years, providing reassurance that catalysts are available that will resist halogen poisoning. Destruction efficiencies of 95 to 99 percent are quoted. High temperature thermal incineration is used to treat vent gases on several VCM plants.

With catalytic incinerators, the catalyst will require safe disposal at the end of its life. Return to the catalyst vendor, at least for precious metal catalysts, is the preferred route. Similarly, any pre-treatment beds would also require safe disposal.



Basis: Ethyl Acetate in air, 70 percent energy recovery

Figure 4.3 Cost of thermal oxidation of VOC stream



Basis: Ethyl Acetate in air, 70 percent energy recovery - No pretreatment

Figure 4.4 **Cost of catalytic incineration of VOC stream**

4.3.5 Adsorption of VOCs from gaseous streams

Adsorption of VOCs is a well established technique with the attraction of the possibility of recovering the organic. By far the most commonly used adsorbent is activated carbon. Others - zeolites and organic polymers - are mentioned at the end of this section.

Removal efficiencies of up to 99 percent are possible with carbon adsorption. This varies substantially between VOC species. A key parameter is molecular weight, which ideally should be in the range 45 to 130. Low molecular weight VOCs are not readily adsorbed, while the large molecules are hard to desorb. Mixtures of VOCs can present a difficulty as some will be selectively adsorbed. Polarity of the molecule and refractive index are also indicators of the ability to be adsorbed.

Adsorbers are vulnerable to choking by dust and often require upstream gas filtration.

With a carbon bed adsorber, flammability is a potential risk. Ketones in particular may undergo partial conversion to peroxides and present a danger of explosion. At high organic loadings in the waste gas, dilution to well below the Lower Explosive Limit may be needed.

For light VOC loading, it can be most economic to discard the carbon when loaded. It can be sent for regeneration or for safe disposal, usually in an incinerator. More usually, the carbon is regenerated in-situ. In typical multibed systems, some beds are adsorbing while other regenerate. Steam is the most common regenerant. Hot nitrogen is also used for regeneration. Nitrogen can be appropriate:

- if the VOC tends to hydrolyse
- to simplify recovery of VOCs soluble in water
- to avoid problems of aqueous pollution.

Regeneration by electrical heating elements is also available when high temperatures are needed for retentive carbons.

Air can also be the regenerating fluid. On an industrial scale, rotary adsorber/desorbers are available from several suppliers. The VOC is adsorbed in one part of the adsorbent bed. As the bed rotates, the loaded adsorbent moves to the regeneration position. Here, the VOC is desorbed by hot air and, usually, fed to an incinerator. Energy from the incinerator can be used to preheat the hot air used for desorption. The activated carbon can be in the form of carbon fibre paper or on a carrier such as corrugated alumina. The rotor can turn around on horizontal axis or, when granular adsorbent can also be used, around a vertical axis.

While activated carbon is the most common adsorbent, others are available. Zeolites are potentially attractive because they are mechanically robust and non-flammable. One disadvantage has been their affinity to water. Suppliers now offer hydrophobic zeolites to address this problem with moist vent gases. Zeolites can be designed to be highly selective for particular species. Rotary adsorber/desorbers are offered with zeolite adsorbents. The main disadvantage compared to carbon is cited as cost by users. Chem Systems was not able to obtain comparative data, however.

Macroporous organic polymers are also available as adsorbents.

Economics

The illustrative economics are calculated on the basis of removal of ethyl acetate from air. Conventional multi-vessel adsorption is used, with regeneration by steam. Included in the costs is a two column distillation unit to recover the ethyl acetate. Data are derived from public domain sources and others including an adsorption equipment supplier.

Table 4.10 gives the cost of removal of VOC for this example. No credit is shown for the recovered VOC. An impure mixture may be used only as fuel, giving a credit of perhaps £50 per ton. If a usable solvent is recovered, the credit depends heavily on the particular material. A range of £300 to £600 per ton is typical for oxygenates supplied in bulk; higher prices may apply to medium scale users.

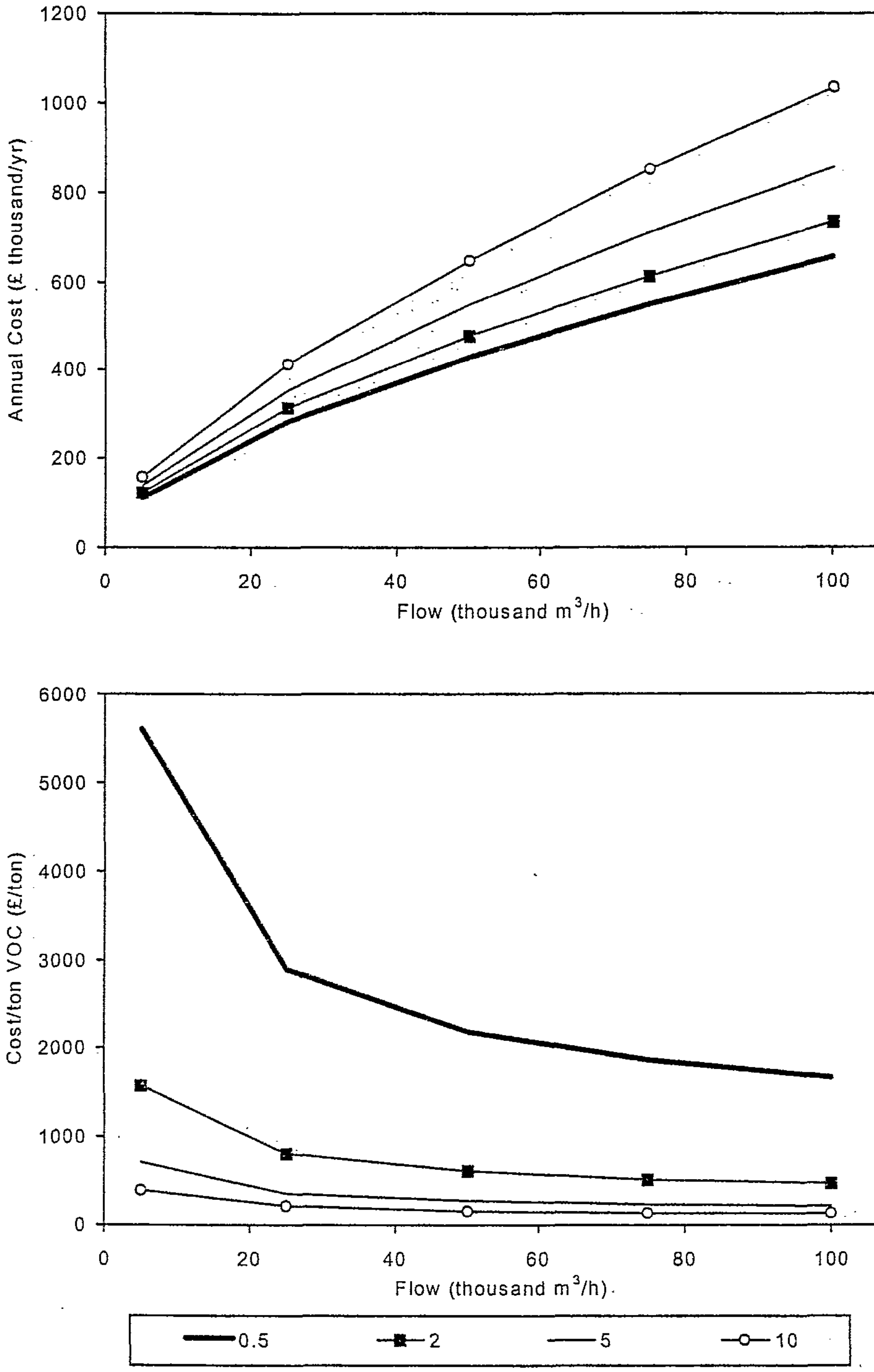
Table 4.10 Cost of adsorption of VOCs from a typical gas stream [1)]

Capital cost	*(£000)*	1 450
Operating cost	*(£000 per year)*	80
Capital charge	*(£000 per year)*	235
Annualised cost	*(£000 per year)*	315
Cost per ton VOC recovered	*(£/ton)*	800

1) Volume 25 000m^3 per hour
Organics: 2g/m^3 ethyl acetate

The costs of steam and power are significant, but capital is particularly important in this example. The type of VOC can significantly affect the materials of construction and so the capital costs.

On Figure 4.5 the effect of capacity and VOC concentration is shown.



Basis: Ethyl Acetate in air, No credit for product shown on graphs

Figure 4.5 Cost of removing VOC by carbon adsorption

Environmental Impacts

The main possible source of secondary pollution is aqueous effluent arising from steam regeneration. Steam use is typically of the order of three kilograms per ton of VOC. With VOCs that are miscible with water, such as ethyl acetate, the organic may be distilled from the water to meet a defined effluent specification. There may be complications, such as the addition of caustic to minimise hydrolysis in the example of ethyl acetate.

Insoluble VOCs, such as many chlorinated hydrocarbons, can be recovered from the steam condensate by phase separation. The water will then be contaminated by traces of organic and may require treatment before disposal. One option, used in metal degreasing equipment in Germany for example, is to regenerate steam directly from the condensate in a closed loop system.

Regeneration with hot nitrogen avoids the production of aqueous effluent.

4.3.6 Condensation of VOCs from gaseous streams

When the partial pressure of a compound in the gas phase exceeds its vapour pressure, it condenses. Condensation can be effected by increasing the pressure, reducing the temperature, or a combination of the two.

Because compression of gas is costly, the most common technique is to lower the temperature. One exception is in the Brayton cycle, where the waste gas is the thermodynamic fluid in a pressure-temperature cycle. This is most applicable to recovery of solvent from drying oven vents. Pressure may be used also in gasoline Vapour Recovery Units (VRU) in addition to temperature reduction.

Cooling of the gas stream is usually achieved by the use of a cooling medium. The temperature required depends upon the relationship between vapour pressure and temperature of the VOC, and the composition of the gas stream. Cooling with water typically achieves 15-20 °C and chilled water cools to around 7 °C. Chilled brine may be used for lower temperatures, down to around -34 °C. For even lower temperatures, the gas must be cooled against a refrigerant which may itself be cooled in a pressure-temperature cycle. Ozone depleting CFCs are being phased out; other refrigerants include HFCs, ammonia, and light hydrocarbons.

Typical applications on condensation are the VRUs mentioned above for controlling tank vents, and reflux condensers on reactor vents or metal degreasers. Reflux condenser applications are usually not likely to meet the emission standards of other techniques unless very low temperatures are used.

Environmental impacts of condensation are generally low, apart from the use of energy for refrigeration. If a low temperature refrigerant is used, the use of CFCs should be avoided. In this sub-section of the report, condensation is regarded as that achieved by indirect contact with the cooling medium. Liquid effluents therefore do not arise.

One option for refrigerated condensation, marketed by BOC, uses liquid nitrogen to provide the 'cold'. The system is best suited to sites where liquid nitrogen is the source of gaseous nitrogen, used for inerting purposes. The gas stream, with VOC, is cooled against evaporated nitrogen and directly against liquid nitrogen. The nitrogen passes to the vessels which it is blanketing, and returns laden with VOC to the condenser.

There are two potential difficulties with refrigerated condensation. Firstly, some materials are likely to freeze, including water vapour. The BOC system uses duplex condensers to overcome this, with one on line while the other thaws. Secondly, fog can be produced. Careful design is required to ensure that the temperature profile in the exchanger minimises fog formation.

Economics

The illustrative economics in Table 4.11 are derived from data quoted by BOC for a cryogenic system using liquid nitrogen. The vent stream was loaded with chlorinated hydrocarbons – mostly methylene chloride – and other solvents at up to 1 500kg per hour in an air stream of 8 000m^3 per hour. The organic loading is around 275 tons per year. One of the interesting aspects of this case is that the volume of the stream was reduced by a factor of ten by converting from air-based to nitrogen-based venting. The reduction is possible because the constraint of the explosion limit is removed in an inert system. The capital cost includes the cost conversion.

TABLE 4.11 Cost of cryogenic condensation [1)]

	Capital cost *(£000)*	**Operating cost** *(£000)*	**Annualised cost** *(£000/pa)*	**Cost per ton VOC** *(£/ton)*
Organic condensation	5 600	580	1 490	5 400

1) Case described above

This is a demanding duty with a high peak load. Thermal oxidation and carbon adsorption were both shown to be significantly more expensive for this case. With thermal oxidation, there would be a substantial running cost associated with scrubbing of HCl.

Environmental performance

The efficiency of condensers based on chilled water or brine is typically 50 to 90 percent, often insufficient to meet IPC guidelines. With refrigerated condensers, the removal efficiency can exceed 99 percent. If liquid nitrogen, with a boiling point of -196 °C is the refrigerant, the IPC guidelines can be met for many compounds.

There are few environmental side effects.

4.3.7 Control of gaseous VOC emissions by absorption

Absorption of compounds from a gas stream into a liquid medium is a widely used unit operation. The absorption device may enhance the mass transfer characteristics by a number of means. These include venturi scrubbers, packed columns, columns with plates or trays, and spray towers.

The absorbent may be aqueous: water itself, dilute acid, or dilute caustic. Aqueous systems are used in numerous applications in the chemical and pharmaceutical industries. Efficiencies of up to 99 percent removed are quoted. This is highly dependent on the physical properties of the VOC, including solubility in the absorbent, and the design of the contact device. One plant operator quoted a 99 percent efficiency for isopropanol and 85 percent for benzene in the same scrubber, because of solubility differences. One possible problem is disposal of the loaded absorbent. It may be feasible to reuse the liquor directly in the process. Otherwise, treatment before disposal would be an integral part of the control technology.

Treatment of absorber wastes could include:

- Removal from the liquid for re-use or incineration. The VOCs can be removed in the gas phase, as with distillation or pervaporation. Alternatively, they can be removed in the liquid phase by activated carbon or by membrane concentration.

- Destruction by techniques such as a conventional biological wastewater treatment plant. More powerful oxidation processes include the use of strong oxidising agents such as hydrogen peroxide or ozone, wet air oxidation, or supercritical water oxidation.

Instead of a once through absorption systems, an absorption-desorption process can be employed. This avoids the effluent disposal problem and the desorbed VOC is recovered in concentrated gaseous form.

Organic liquids can be used as absorbents. For example, VCM may be scrubbed in organics such as EDC or MEK in recovery systems.

The Ceilcote system is based on a high molecular weight organic liquid as absorbent. The technology suppliers claim references in a range of industries, including paint manufacture, pharmaceuticals and textiles. The removal efficiency depends on the VOC. For toluene and xylene, a removal efficiency of 97-99 percent is feasible. For methylene chloride, it is only 86 to 91 percent.

Absorption is, in general, regarded as appropriate for high concentrations of VOCs. Although removal efficiencies of up to 99 percent are quoted for specific applications, a figure of 95 percent is more usual. Absorption often cannot meet the vent gas quality achieved by other techniques such as incineration or adsorption. For the Cool Sorption system, for example, an additional adsorption unit may be fitted to meet the TA Luft standards.

Environmental Impacts

Secondary pollution from a once through aqueous systems consists of:

- loss of absorption liquid as droplets or vapour in the treated gas

- treated wastewater, containing VOCs to the quality level required by the regulatory authority, possibly with saline load if the absorbent contains chemical reagent
- products of wastewater treatment, such as excess activated sludge or loaded activated carbon.

The secondary pollution from closed loop absorption systems is low. It could include:

- loss of absorbent as droplets or vapour in the treated gas

- losses of the heavy organic absorbent as liquid : expected to be minor and to pass to the site wastewater system

- pollution associated with raising steam and using power.

4.3.8 Treatment of gaseous VOC streams with membranes

Membranes can be used in the treatment of gaseous streams that contain VOCs. The VOC concentration of the permeated material is higher than that in the original stream, permitting condensation or other treatment. If the remaining air is not of acceptable quality for discharge, it can pass to a second membrane step. Permeated air from the second step would return to the inlet of the first membrane stage. Another variant is needed if the VOC waste stream is very dilute. In this case, a second membrane stage may be needed to concentrate the VOC to a level at which it can be condensed or treated.

A specific example is described below for the recovery of chlorinated hydrocarbon VCM (vinyl chloride monomer).

Description

The process reviewed is that offered by MTR (Membrane Technology and Research) of Menlo Park, California. The process is named Vapor Sep. Key to the process is a membrane that is more permeable to organic compounds than to inorganic gases.

Technical details of the membrane are proprietary information. In general, the membranes consist of a rubbery polymer layer cast on a tough microporous support. The polymer layer is very thin at 0.2 to 5 microns, and acts as the separating agent. The microporous support material, made of an engineering resin, provides mechanical strength. It is not prone to block since the feed is exposed only to the rubbery layer.

Membrane polymers could be materials such as polysiloxane and polyolefins. The solubility of organic vapours in rubbery materials is 10 to 100 times higher than that of inorganic gases such as oxygen and nitrogen. The organic compounds diffuse more slowly in the polymer because of their larger molecular size, however. Diffusivity of organic compounds is typically 1/10 to ½ as large as that of inorganic gases. Permeability through the membrane is the product of solubility and diffusivity, so the net effect is a higher permeability of organics. The concentration of VCM in permeate is typically ten times that in the feed gas, when the latter is relatively dilute.

The driving force for the separation is the pressure drop across the membrane, which could be provided by a vacuum pump on the permeate side.

Recovery of the organic compound from the gas stream can be 90 to 95 percent in a single stage. The permeate can be treated by compression and condensation to recover the organics. In the case considered for VCM recovery, the permeate is returned to the main VCM vent stream.

One operational advantage is reported to be a tolerance to intermittent and fluctuating loads. The membranes can withstand temperatures of up to 60°C. MTR's technology is installed in over ten plants for the recovery of halogenated organics, including several installed in VCM separation applications.

The case considered is the recovery of VCM from a condenser vent stream. The stream flow is 40Nm^3/hour at 4.5bar, with 32.5 percent v/v of VCM.

Six membrane modules required for the single separation stage. The modules are spiral-wound, with layers of membranes wrapped around a porous collection pipe. Individual membranes are separated by spacers. The flow pattern is crossflow: feed passes parallel to the membrane surface and the vapours permeate through the membrane perpendicular to the flow. Figure 4.6 illustrates.

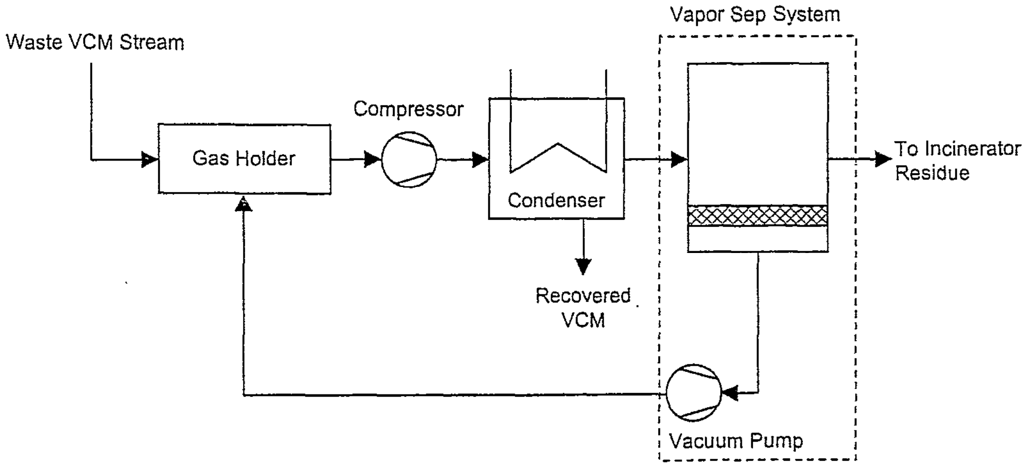


Figure 4.6 Membrane separation of VCM

The feed gas is under pressure. Additional driving force is provided by a liquid ring vacuum pump, which moves the permeate back to the gas holder.

VCM is reduced from 32.5 percent v/v in the feed to 2.5 percent in the treated gas. This represents a recovery of around 95 percent. Although the VCM permeates more rapidly than the inert materials, there is still significant flow of the latter. The total feed to the membrane modules, allowing for recirculation of intert materials, is around 3.75 times the original stream. In terms of total load on the compressor and condenser, this is usually not significant, and it is assumed that these need no modification.

The system is supplied as a skid-mounted unit containing the membrane modules, the vacuum pump, and control and sampling points. Membrane modules have an estimated life of three years, after which they need replacement.

Economics

Illustrative economics are shown in Table 4.12. No credit is shown for recovered VCM as the correct basis depends upon the nature of the operating company. If the market price of VCM is used (NW Europe contract Q4 1997), the unit would show a net cost of around £15 000 per year, or around £53 per ton recovered. For an integrated facility the credit would be less and the net cost larger.

TABLE 4.12 Recovery of VCM by membrane separation

	Recovery *(%)*	**Capital cost** *(£000)*	**Operating cost** *(£000/pa)*	**Annualised cost** *(£000/pa)*	**Cost per ton** *(£/ton)*
Membrane separation	95	280	31	110	400

4.3.9 Biological treatment of VOCs in gaseous streams

Many organic compounds can be decomposed aerobically by microorganisms to produce carbon dioxide, water, and other products. There are two basic types of process: biofilters and bioscrubbers.

Biofilters

The micro-organisms are settled on a solid carrier material. This may be compost, fibrous peat, or heather. Other materials such as lava or porous clay may be used to provide an extended inner surface area for the microorganisms to inhabit. Pollutants in the air are sorbed onto the surface of the carrier material and decomposed by the microorganisms.

The microorganisms are normally those present in biological carrier material. These can be enriched or, for inorganic carriers, supplied by adding sludge from sewerage treatment or similar. Nutrient addition may also be needed. The system is susceptible to shock loads, although can usually acclimatise to gradual changes in pollutant type and quantity. Prior dedusting and humidification of the feed gas stream is also recommended.

Biofilters typically occupy a large plan area, but can be designed in layers to partially overcome this.

Processes using biofilters include many where the major problem is smell, such as rendering plants and sewerage treatment facilities. Other applications include some chemical plants and steel foundries.

The performance of biofilters varies from very low, at around 20 percent, to removal beyond the point of detection. The VOC concentration in the inlet gas is typically low, but is over 800 mg/m^3 in some examples quoted (VDI Richtlinien 3477).

There are few secondary pollutants associated with biofilters. If dust is removed upstream, it will require disposal. The carrier material itself also needs occasional replacement.

Bioscrubbers

With bioscrubbers, organic compounds are absorbed from the gas stream into water. The absorbed compounds are aerobically decomposed by micro-organisms that are either suspended in the water or form a biological mat inside the scrubber.

Suspended systems require an additional activated sludge tanks to allow for the slow rate of biological degradation. If large, these tanks must be aerated. As with a conventional wastewater treatment plant, these systems produce an excess activated sludge waste for disposal.

The other type of bioscrubber is a percolating filter installation, where the microorganisms have colonised the internals or packing of the scrubber to form a biological mat. Percolating filter installations have a large surface area over which the loaded scrubbing water is distributed.

Both types of bioscrubber need nutrients to be added to the water.

Biological Treatment: Summary

Biological treatment is particularly suited to gas streams with low concentrations of VOCs, often constituting an odour nuisance rather than a VOC burden. Removal efficiencies are good at the low concentrations.

The cost of biological treatment is low.

There are minimal pollutants:

- products of degradation, typically CO_2 water and mineral salts
- effluent from any upstream dedusting
- excess sludge from bioscrubber with microorganisms in suspension.

4.3.10 Fugitive emissions of VOCs

A significant proportion of emissions from plants handling VOCs arises from leaks from equipment and fittings. Main sources include valve seals, particularly on gas or vapour duty but also, to a lesser extent, from valves handling light liquids or two phase flows. Seals around the shafts of rotating machinery such as pumps and compressors are also important. Losses from flanges, drains and relief valves contribute as well.

Control of fugitive emissions takes two main approaches. The first is to select equipment and fittings of high integrity; the second to improve maintenance procedures.

Description: high integrity design

Elements of high integrity design include:

- minimisation of the number of flanges, to the extent that this is consistent with the needs of maintenance
- use of low-leakage valve stem packings
- minimisation of losses from shaft seals of rotating machinery.

Low-leakage shaft seal systems include double or tandem mechanical seals. However, sealless pumps are also available. They include canned motor pumps, in which the motor is contained within the pump housing, and magnetic drive pumps where the energy is transferred by magnetic coupling. These types of pump are generally of higher capital cost than conventional pumps with double mechanical seals. Typical ratios quoted, related to conventional pumps, are around 1.3-1.5:1 for magnetic drive and 1.7-2.2:1 for canned pumps. Power consumption, too, is higher by 10-20 percent because of drive losses. However, users of sealless pumps remark on the low frequency of maintenance compared to sealed pumps. The main source of failure on sealless pumps is the bearings. For sealed pumps, the seals need replacement and any lube system must be maintained. If a leak detection system is required, the total capital and operating cost of a sealed pump is quoted by some users as comparable to that of a sealless unit.

Description: operation and maintenance

Monitoring and maintenance procedures are often termed LDAR, or Leak Detection and Repair. Leakages are detected by monitoring devices and, if the leakage exceeds specific levels, repairs must be carried out. There are various levels of LDAR. For convenience two levels are defined below, drawing on refining industry experience and comments from a UK petrochemical plant operator.

- Level I: annual inspection of gas and volatile liquid service components
- Level II monthly leak detection and repair.

Other operational measures in Level II include the capping of open-ended lines and use of closed sample purge systems.

Economics

It is difficult to quantify the cost of high integrity design as the incremental cost is often hidden in other costs of plant modifications.

For LDAR schemes a broad estimate of costs is shown in Table 4.13. The reduction of VOC losses is taken as 60 percent for Level I and 70 percent for Level II, based on work performed by the US EPA on refineries. The quantities of VOCs, and therefore the cost per ton abated, are very approximate. The basis is a plant handling 20 000 tons per year of gaseous hydrocarbon streams and 30 000 tons per year of liquid.

TABLE 4.13 Cost of containment of fugitive VOCs (2)

Technique	Capital cost *(£000)*	Net operating cost *(£000 pa)*	Annualised cost *(£000 pa)*	Cost per ton VOC *(£/ton)*
Level I	20	8.5	12	760
Level II 1)	80	38	51	19 600

1) Incremental
2) Plant handling 20 000 tons per year gases, 30 000 tons per year liquids

The initial stage of LDAR is, in the case examined, a cost-effective measure while the more rigorous testing regime is poor value for money. Most of the annualised costs are labour related.

Minimisation at source of VOC emissions

In general, many processes in which VOCs are emitted are those employing a solvent. This applies to the application of formulated products such as coatings, adhesives, and printing inks. It is also true of many processes in which chemical products are produced, such as pharmaceuticals and other fine chemicals and, of course, chemical products that contain solvents.

When solvent is used as a carrier, there are fundamental process options to reduce or minimise its use. Coating applications provide a good example, where the options include:

- high efficiency transfer devices (ie spray equipment)
- high solids/low solvent coatings
- water-based coatings
- dry coatings
- uncoated products, such as aluminium car bodywork.

For the processes reviewed here – the petrochemical and large scale organic processes – the use of solvents is less prevalent. Where they are used there may be opportunity for replacement. Bayer has replaced benzene with cyclohexane solvent in rubber production, for example. Usually however, the organic compounds are part of the feedstocks and other process streams involved in the production of the product, or arise as waste or co-products. Fundamental reduction techniques are therefore not necessarily applicable.

General principles may be noted, however.

- In some processes, there may be a choice of feedstock. Feedstocks with a desirable specification will give a higher yield of the required product. They will also contain lower quantities of impurities, such as sulphur, that might give rise to emission of inorganic pollutants. Purchase of a high specification feedstock may shift the purification duty to the supplier. If the supplying plant is a large integrated facility, such as a refinery or petrochemical complex, it may be better suited to perform such purification. When it is feasible to consider different feedstock qualities, such as on a new plant, the issues may be more complex than a simple price differential. Supply and demand, and the close integration of petrochemical industry in general, will constrain the possibilities.

- Catalyst design is important. A low yield per pass is not desirable, and requires substantial recycle. This has implications in cost and, typically, power use. More directly relevant is the selectivity. Low selectivity results in production of unwanted co-products that can be potential pollutants. Catalysts are specific to each process. The possibility of retrofitting an existing plant with a newer generation of catalyst should be considered where possible. Where the catalyst system is dispersed in the process medium, a highly active catalyst will require less 'ash' removal and associated treatment needs. This applies to recent developments in polypropylene technology, for example.

- Where waste products or co-products also occur, emissions can be minimised by recovery and recycle. A purge of paraffinic hydrocarbons from a polyolefin plant recycle loop, for example, may be treated in several ways. One is to flare the purge or, preferably, to use as fuel. Ideally the purge can be recycled to join the feed to a cracker on an integrated site. The decision on whether to use as fuel or try to recover useful process streams is often complex, on environmental, regulatory and economic grounds. The possibility of recycling will be enhanced if streams of dissimilar composition are kept segregated. It should however be recognised that the use of by-product streams as fuel is integral to the economics and integration of many petrochemical processes.

- Losses of VOCs may occur on occasions when the equipment is opened. Reference to appropriate maintenance procedures is made in section 4.2. In some processes there is a regular need to open up, such as to descale reactors. Appropriate process design can minimise this need. For example, anti-caking chemicals can be sprayed automatically inside vessels. Cleaning systems can be designed with filter sprays so that the equipment does not need to be opened. PVC plant design (see Section 5) is an illustration of this.

- VOC material may be lost into cooling water or process water and then evaporate into the atmosphere. This can be minimised at the design stage by avoiding direct contact where possible of water and gases that contain VOCs. This can occur in column condensers or in vacuum ejector systems. Where VOCs do report to a water stream, options can include recovery of VOC by stripping or solvent extraction, for example. An alternative or supplementary technique is to recirculate the contaminated water for re-use.

- If the organic material is a main feedstock or product, there is usually a strong economic incentive to minimise inventory. It should also be noted that losses from tankage are influenced by throughput and movements of material as much as by the volume held. However, it is generally good practice to minimise holdings, particularly where the material is, for example, make-up to a recirculating solvent system.

4.3.12 Abatement of pollution from combustion

Combustion processes, as defined in the Environmental Protection Act (Prescribed Processes and Substances) Regulations 1991 (1991 No. 472), as amended, are covered by separate guidance notes. However, some combustion operations are integral parts of petrochemical and large scale organic plants. Cracker furnaces are an example. The requirements for a particular temperature profile for the reactor tubes and dimensional constraints in the design can limit the possibilities of abatement.

The following summary is provided for completeness. Some combustion devices are those used for control of VOC emissions; these are considered elsewhere.

Emissions of $S0_2$

For large scale petrochemical and organic processes, Chem Systems identified no evidence of plants using any form of the gas desulphurisation (FGD) or in-furnace addition of reagent. If a high-sulphur fuel stream must be burnt it would probably be directed to the site boiler (a 'combustion process') where economies of scale may support FGD.

However, Chem Systems notes that there are few instances of FGD even on refineries world-wide in spite of the need to dispose of high sulphur residues. Seawater scrubbing, the regenerative Wellman-Lord process, and gasification are installed, or intended, in some locations. The vast majority of refineries, however, control their SO_2 emissions by fuel selection and management. Low sulphur fuel oil, gas oil, or natural gas are used to comply with site bubble limits. The same approach appears to be adopted by large petrochemical facilities.

The cost of fuel selection consists of:

- investment cost of converting burners and furnaces if needed
- the change in cost per unit of energy consumed from using a different fuel
- possible cost implications if a high-sulphur stream must now be exported.

The cost of a fuel switch from high sulphur fuel oil would be around £300 to £500 per ton of SO_2, resulting from differential fuel prices. The other cost elements are site specific.

Other options for reduction of $S0_2$ emissions are summarised in qualitative form on Table 4.14.

Table 4.14 End of pipe SO_2 control

Technique	Reagent	Waste/by-product	Typical efficiencies *(percent)*
In-furnace injection	Lime, sodium bicarbonate	Solid residues	40-60
Semi-dry spray tower	Lime, sodium bicarbonate	Solid residues	65-85
Limestone - gypsum	Limestone	Gypsum – can be commercial grade	95
Wellman-Lord (regenerative process)	Sodium hydroxide/ sodium sulphite	Concentrated SO_2 (eg acid plantfeed). Aqueous thiosulphate purge	95
Scrubber, alkaline (not regenerative)	Sodium hydroxide	Sodium sulphite liquor	95
Scrubber, seawater	Seawater	Neutralised seawater	90-95

Emissions of NOx

Control techniques for NOx are usually divided into those involving a modification to the combustion process and those in which the NOx is removed after it has formed.

One further option, not considered in detail in this report, is to switch to natural gas. This would result in a significant reduction in NOx emissions. The use of natural gas with the control techniques described below would, by a strict definition, be a Best Available Technique for NOx control.

a) Combustion modifications

The basic objectives of combustion modifications are to reduce temperatures and to reduce the available oxygen. This will directly reduce the thermal NOx; the impact on fuel NOx is less dramatic.

Control of excess air is an important factor. A one percent reduction in excess O_2 leads to a NOx reduction of typically around six percent. More accurate control is generally possible with mechanical draft heaters than natural draft designs. Because control of excess air is relatively inexpensive and has advantages in heater efficiency, it is expected that this is a standard operating procedure.

Combustion air preheat also has a significant impact. Preheating air to 250°C may roughly double NOx production, for example. It may be possible to reduce preheat on some heaters and compensate by extra heat exchange in the convection section.

The main add-in technical modifications are reviewed below.

- **Low NOx, Burners (LNBs)**

There are two basic types of Low NOx Burners: staged-air and staged fuel designs.

In the staged-air burner, the initial combustion occurs in a fuel-rich reducing atmosphere so that nitrogen is formed in preference to NOx. This means that there is some reduction in the production of fuel NOx as well as thermal NOx. Total reduction efficiencies are typically 30 to 40 percent. A long and less well-defined flame is produced by staged-air burners. This can result in problems with retrofitting and with process control.

A portion of the fuel gas is injected into the primary combustion region in staged-fuel burners. This results in lean (air rich) combustion that reduces peak flame temperature. The technique is capable of relatively high reductions in thermal NOx. Reductions of up to 70 percent of thermal NOx are claimed (EPA report 453/R-93-015). It is therefore suitable for gas-fired heaters where all the NOx is thermal NOx. Staged-fuel burners can operate at lower excess air levels and have shorter flames than staged-air burners.

LNBs are not always feasible, particularly in a reftrofit. Many process heaters are floor-fired and there may not be sufficient space at the base to accommodate the large LNBs. Where closely spaced burners with a relatively low unit heat release are required, as with reformers or hydrocrackers, there could also be layout problems.

It may not be feasible to install LNBs in duties where high intensity burners are presently used. These, often used for waste burning, use pressurised air and have characteristics of high mixing and short flames. High oil viscosity is sometimes quoted as a difficulty with LNBs. This limitation applies to all steam atomised burners according to one manufacturer.

- **Flue Gas Recirculation (FGR)**

With FGR, around 10 to 30 percent of the flue gas is recycled to the combustion zone. The temperature is reduced and the local oxygen concentration in the combustion chamber is depressed. This reduces thermal NOx formation, but not fuel NOx. With LNBs, flue gas recirculation can reduce NOx by around 55 percent.

FGR is appropriate for mechanical draft rather than natural draft heaters. It has been applied to heaters with a few burners, such as vertical, cylindrical heaters. Steam injection acts in a similar way to FGR.

The use of FGR may increase risk in the case of a process heater tube burst. Furnace gas recirculation is preferred.

- **Ultra-Low NOx Burners (ULNB)**

Ultra-low NOx burners have been designed to meet the requirements of the South Coast Air Quality Management District (SCAQMD) Rule 1109 of the USA. The burners can incorporate various combinations of the techniques used in conventional LNBs. In addition, internal recirculating flue gas (IFGR) and steam injection may be employed. With IFGR, flue gases from the burner are drawn back into the combustion zone by a venturi effect.

Very high efficiencies, of around 75 percent reduction, are claimed for both oil and gas-fired heaters using ULNBs.

Retrofitting problems with ULNBs will be similar to those with conventional LNBs.

- **Radiant Burners**

A gas burner is manufactured that has a cube of ceramic fibres at the burner tip. The fibres act as a catalyst and the combustion occurs at only around 980 °C. This substantially reduces NOx formation. The burner intrudes into the furnace space and so retrofitting is likely to be difficult. Reported problems include fouling, fragility and limited capacities.

b) Flue Gas Treatment

Flue gas treatment techniques are directed at removing or converting NOx after it is formed. The most common methods are those in which the NOx is chemically reduced to nitrogen.

- **Selective Non-Catalytic Reduction (SNCR)**

At high temperatures, the NOx may be chemically reduced to nitrogen without a catalyst. Chemical reagents include ammonia (anhydrous or aqueous) and urea. Other chemicals such as hydrogen or methanol may be used to extend the temperature at which conversion occurs.

Possible technical disadvantages with SNCR are with ammonia slip, if the NH_3:NOx ratio is not optimised, and formation of ammonium sulphate or bisulphate if oxides of sulphur are present. Possible formation of nitrous oxide, N_2O, is also cited as a disadvantage of SNCR.

The reagents are injected into the combustion chamber or flue gas system at a position that corresponds to the appropriate temperatures. Distribution is usually aided by air or steam. Retrofitting can be relatively simple but there may be difficulties with specific heater configurations and temperature profiles.

The Exxon Thermal DeNox process is based on ammonia injection. The allowable temperature range for ammonia is 870 to 1 100°C. With the addition of hydrogen, the temperature range may extend to 700 °C.

Urea based systems, offered by Nalco Fuel Tech and by Noell KRC, can further extend the temperature range down to around 550 °C by the use of additional chemicals. The storage and handling of urea generally requires fewer precautions than that of ammonia.

The potential reduction efficiency for SNCR is around 50 to 70 percent. In practice, the technique is usually applied in combination with low NOx burners or other combustion modifications.

- **Selective Catalytic Reduction (SCR)**

The SCR process involves the injection of ammonia, usually with steam or air for distribution, into the flue gas system of a catalyst bed. As with SNCR, the NOx is chemically reduced to nitrogen. However, the use of the catalyst permits the reaction to occur at lower temperatures than with SNCR. Operating conditions range from 230 °C to 630 °C depending on catalyst; a range of 315 to 370 °C is typical.

As with SNCR, there are possible problems of ammonia slip and the formation of ammonia salts. A lower NH_3:NOx ratio is used than with SNCR, however.

On new plant, the SCR may be installed in the 'high dust' position corresponding to the appropriate temperature window in the flue duct. If the SCR is installed in a tail gas position, heat exchange capacity and supplementary fuel will probably be needed to achieve the correct temperature. The tail gas position may be more convenient for retrofits.

In the case of fired heaters, an appropriate temperature window often occurs downstream of the firebox. It is necessary to take flue gas at the appropriate temperature and route it through the SCR before returning it to the stack. The significant pressure drop through the SCR system, of 25 to 125 mm water gauge, requires the installation of additional fan capacity. A natural draft heater would thus require conversion to mechanical draft operation.

The space requirements are significant. A typical 25 to 30 MW heater needs a plot of 4 x 5m for the reactor and a further $6m^2$ for catalyst removal and replacement. Facilities to store the ammonia are also needed.

As with the other techniques, it is not always feasible to retrofit SCR. In addition to space constraints, there might not be an appropriate temperature window.

The incremental cost of installing Low NOx Burners (LNBs) are relatively small on a new plant, but more significant and variable on larger plant. Flue gas treatment processes are more expensive, and there may also be loss in thermal efficiency resulting from the need to distribute gas over the treatment zone. LNBs are generally accepted as good practice except where there are process or physical configuration problems. For the purposes of the economic review (Section 6), two NOx reduction techniques are considered: SNCR and SCR. This is because these techniques provide an example of BAT, where the cost differential with normal practice is significant. Chem Systems is aware that SCR has been required in the conceptual project stage for new steam crackers in Germany, but has not identified plants to which it is actually fitted.

Table 4.15 Cost of flue gas treatment for NOx control

		SNCR	SCR
NOx reduction	*(%)*	60	75
Capital cost	*(£000)*	540	1865
Operating cost	*(£000 per year)*	84	114
Annualised cost	*(£000 per year)*	171	417
Cost per ton NOx	*(£/ton)*	3 565	6 949

Basis: Flue gas stream from 40MW fired furnace

4.3.13 Water treatment

Often, waste water is treated in a site effluent facility that provides a service for several processes. Many of the techniques used for water treatment are standard. They include phase separation, mechanical filtration, pH adjustment, other physio-chemical treatment, and biological treatment. Conventional waste water treatment plant with these elements can handle a variety of wastes. Even with organic pollutants that are difficult to degrade, it is often possible to develop biomass to handle it.

In this review of selected techniques, the focus is on applications where conventional technology is not adequate. The techniques selected are those appropriate for:

- treatment of moderate to high concentrations of difficult organics
- treatment of effluent with low quantities of halogenated waste
- removal of significant loads of dissolved salts.

Case A: High Organic Loading

Conventional aerobic or anaerobic biotreatment may not be technically suitable for streams containing organics at high concentrations – half a percent or more for example – or organics that are both difficult to degrade and toxic. This type of waste is more characteristic of fine chemical production than of petrochemical and large-scale organic processes. However, there are instances where it applies, such as nitrobenzene/aniline.

Possible technologies include:

- thermal incineration
- wet air oxidation
- supercritical water oxidation.

a) Thermal incineration

The thermal incineration option is conventional technology, employing a fixed combustion chamber(s) possibly with an after-burner. The required combustion conditions depend upon the type of organic pollutant. The main disadvantages of incineration is economics. The total aqueous effluent must be evaporated and raised to the combustion temperature. Fuel is needed, and must be sufficient to also raise the combustion air and secondary air to the required temperature. Heat recovery is possible, but may in some cases prejudice the control and the ability to maintain an appropriate temperature profile. Fuel costs can therefore be significant unless a high energy content CV waste stream is also available that would not find a commercially beneficial use.

The other disadvantage is the atmospheric emissions resulting from burning the fuel and the pollutant. Secondary contaminants may arise if the waste stream contains, for example, sulphur.

b) Wet air oxidation

Wet air oxidation breaks down the organic content of wastes by a combination of hydrolysis and oxidation at sub-critical conditions. The basic technology has been employed since the 1950s, initially applied to brown liquors from pulp and paper mills. There are several variants to the process.
In the Zimpro process, both air and waste water are pumped to the operating pressure of up to 200 bar. The stream is heated to around 300°C in heat exchangers which recover heat from the treated stream and also use an auxiliary fuel or energy source. Off gases arising from let down consist largely of CO_2 and water from the destruction of the organic. Gas treatment may be needed if acid gases or particles are present.

A catalyst is used in the Bayer process, permitting lower temperatures and pressures to be used.

A residence time of around one hour is typical. This implies a large (for the flow) pressure vessel constructed of stainless steel or possibly, if halides are present, clad with titanium.

Possible operating difficulties have been reported as choking with solids contained in the waste water feed, and corrosion arising from halides. This is dependent on the design of the unit and on the application.

Typical efficiencies of break down are around 97 percent. It is common for waste water from wet air oxidation to pass to a conventional site system for polishing.

c) Supercritical water oxidation

Higher destruction efficiencies are possible with supercritical water oxidation (SCWO). A fluid is considered supercritical if its temperature and pressure both exceed their critical values. For water, the critical conditions are 374 °C and 221.3 bar. Supercritical fluids exhibit properties that do not correspond to those of either gases or liquids. Supercritical water has a density high enough to permit reasonable process throughputs to be achieved, but with gas-like transport properties. Above the critical point, the hydrogen bonding in water is essentially eliminated and the fluid ceases to be a polar solvent. The solubility of organics increases dramatically; that of inorganic salts drops sharply.

When oxygen is added to aqueous solutions of organic contaminants under supercritical conditions, the complete miscibility and enhanced reaction kinetics can result in high combustion efficiencies. Depending on the conditions and residence time, destruction of over 99.99 percent is possible.

In a typical SCWO process, the aqueous waste is pumped to operating pressure, and compressed air can be the source of oxygen; alternatively, oxygen itself may be used. The technique is most appropriate for relatively concentrated wastes, at say 10-35 percent. Outside this range, dilution or additional fuel may be needed. A caustic supply is necessary to neutralise mineral acids such as hydrochloric acid, where formed in the destruction reactions. Corrosion by chlorides is a possible problem.

After oxidation, the salts are removed as brine. An important part of the development effort has been to solve potential problems of scaling by deposited inorganic salts, and to avoid the need to remove solids from a high pressure reactor. A possible solution is a two zone reactor with an upper zone at supercritical conditions and a lower zone which is cooled to subcritical temperatures. The inorganics that precipitate from the supercritical zone drop into the liquid phase where they are dissolved or form a slurry that can be removed by pipe. Partial recycle of the reaction products raises the temperature of the feeds: reaction occurs at typically 600 °C -650 °C and 250-275 bar.

The hot reactor products are cooled, raising steam and providing further low grade heat if required. Liquid and vapour phases can now be separated in several stages of pressure let-down. The off-gases are carbon dioxide, water vapour, excess oxygen, and nitrogen. Some energy recovery should be possible on pressure let-down.

A reaction time of 30 to 60 seconds is typical, which implies a lower reactor volume than for wet-air oxidation, even allowing for density differences. However, comparatively expensive materials of construction, such as Incolloy 625, are used even for streams containing no halides.

Extensive development has been undertaken on SCWO, particularly in the United States. Technology suppliers include the Modell Development Corporation, known as Modec, Eco Waste Technologies and Modar. The process is reported to have been installed in Texas to treat organic wastes from ethylene production. In Europe, trials have focused on the possibilities of treating halogenated wastes.

Economics

Economics are given on Table 4.16 for a typical case. The flowrate in the typical case is 5m^3 per hour and the organic concentration is 0.5 percent, taken to be phenol for the purposes of stoichiometric calculation.

Table 4.16 Cost of treatment of a high-organic effluent [1]

Technique	Capital cost *(£000)*	Operating cost *(£000 per annum)*	Annualised cost *(£000 per annum)*	Unit cost *(£/m^3)*
Incineration	4 000	1 750	2 400	60
Wet air oxidation	5 000	360	1 170	29
Supercritical water oxidation	7 000	690	1 830	46

Note 1) Volume 5m^3/hr aqueous affluent
Organics at 0.5%

For the case considered, wet air oxidation offers the cheapest solution. All of the techniques involve significant capital and operating costs.

Case B: Dilute halogenated wastes

The environmental impacts of certain pollutants may be so serious that very high removal efficiencies are required. Various heavy metal compounds could fall into this category, and certain halogenated compounds. This category of pollutant is not, in general, characteristic of petrochemicals and large scale organics. However, there are instances both of catalyst loss, for example, and halogenated organics in effluent in the EDC/VCM/PVC chain (see Section 5).

The techniques selected for review are those designed to treat low concentrations of halogenated organics in aqueous effluents. Higher concentrations may be addressed by different techniques, including stripping and recovery.

Two techniques are reviewed: the use of granulated activated carbon in the aqueous phase, and a UV/ozone/hydrogen peroxide system. A typical case is considered, with a flow of 45m^3 per hour and a concentration of halogenated organic of 5mg/litre. The organic is taken to be tricholoroethylene, and the required removal efficiency is 99.98 percent. This is a stringent requirement that implies that the receiving water body may be a source of drinking water.

Granulated Activated Carbon (GAC)

This is comparatively conventional technology. To achieve the required reduction, two stages of beds in series are needed. The bulk of the removal of the containment would be achieved in the first stage. The second stage would act as a polishing unit and a guard unit should breakdown from the first stage occur. The design is based upon the first stage vessels in parallel, followed by one second stage vessel.

Any contamination such as grit imposes further requirements on the design. Rather than carbon derived from coconut shells, which could be prone to blocking, a coal-based carbon would be used. In addition, the first stage beds are periodically backwashed to remove contaminants of this sort. The backwash water returns to the reservoir of untreated effluent.

At the low concentrations of trichloroethylene, in situ regeneration is unlikely to be economical. The unit would be sized to run for around two months before the bed would need to be changed. Disposal options include regeneration by an external contractor or incineration. With over 5 weight percent trichloroethylene, the spent carbon would not be suitable for landfilling. Regeneration, usually performed at high temperatures, results in a significant carbon loss and widening of the pores. This reduces its effectiveness as an adsorbent. Incineration would need to be performed in a high temperature incinerator, designed to take halogenated organics. The spent carbon has a high calorific value and depending on the pricing philosophy of the merchant incinerator, this could result in a relatively low cost disposal cost. In the estimate of the economics of treatment, it is assumed that the spent carbon is sent to incineration at a total cost of £300 per ton including haulage.

UV/Ozone/Hydrogen Peroxide Treatment

Either ozone or hydrogen peroxide can be used as oxidising agents to decompose organic pollutants, perhaps as a partial treatment step before biological treatment. Ultraviolet light, combined with either or both of these chemicals, produces a significantly higher oxidising power.

The mechanisms by which this happens are:

- transformation of ozone or hydrogen peroxide to highly reactive hydroxyl radicals
- excitation of the organic pollutant compound to a higher energy level
- initial attack of the target organic by UV light.

The principle of the process is therefore to add either or both ozone and hydrogen peroxide to the aqueous effluent, and to expose it to UV radiation. The technology evaluated is that developed by Ultrox in Santa Ana, California. The process has been used in several applications, many involving chlorinated compounds in contaminated groundwater or wastewater.

Contaminated water is pumped into a stainless steel treatment tank and hydrogen peroxide is metered into the feed line. Ozone may be generated from air or cryogenic oxygen. With air, an ozone concentration of around two weight percent is achieved; with cryogenic oxygen, the concentration is up to five percent. The air must be dried to a dewpoint of -50°C before the ozone is generated by corona discharge.

The treatment tank is divided into compartments. The gas with ozone is metered into appropriate compartments through stainless steel diffusers. Each compartment is fitted with UV lamps, usually mounted vertically. The effluent passes by gravity through the treatment tank, flowing upward and downward in alternate compartments.

Ozone is itself a potential health hazard; control of emissions of VOCs in general is aimed at preventing the photochemical creation of ozone and other oxidising species. The vent air from the treatment tank is therefore treated in a catalytic decomposer, in which ozone converts to oxygen, before venting.

Economics

The cost of treatment of the typical halogenated stream by the two methods is presented in Table 4.17.

Table 4.17 Cost of treatment of halogenated effluent 1)

Technique	Capital cost *(£000)*	Operating cost *(£000 per annum)*	Annualised cost *(£000 per annum)*	Unit cost *(£/m^3)*
Granulated activated carbon	400	67	132	0.37
Carbon UV plus oxidant	500	52	133	0.37

Note 1) Volume $45m^3$/hr
5mg/litre trichloroethylene

The operating cost of the GAC system is higher than the UV/oxidant system because of the cost of new carbon and of disposal of loaded carbon. The running costs for the UV/oxidant system include hydrogen peroxide and lamps. When the capital charge is taken into account, the cost of treatment is similar for both techniques.

Case C: Dissolved salt

Dissolved inorganic salts are often not of high toxicity on a weight basis. In very large quantities, the effluent can effect the salinity of the receiving water and impose a stress on the aquatic ecosystem. This is more likely to be an issue for inland water than for discharges to sea or tidal estuary.

High dissolved salt loadings are characteristic of inorganic processes rather than, usually, organic processes. Dissolved salts can arise from coagulation systems, such as in some cellulose processes or synthetic rubber production. Often, the process can be redesigned on new plants to avoid the arising.

Possible techniques for removing dissolved salts from effluent include:

- precipitation by addition of a reagent, usually producing a solid waste; this technique often substitutes ions rather than removing them, or affects pH
- removal by membrane systems such as reverse osmosis or electrolysis
- crystallisation of the dissolved salt by chilling, evaporation or both

As an example, indicative economics are shown in Table 4.18 for an evaporative crystalliser fulfilling the following duty:

- effluent flow 27.5m^3 per hour
- sodium sulphate loading 55g/litre
- sodium sulphate removal 70 percent, with product in anhydrous form.

The technology costed employs a two-stage vacuum flash, with the vacuum provided by a steam ejector system, followed by a crystalliser. A steam consumption of around 600kg per ton of evaporation is required. For sale of recovered sulphate, a nominal netback credit of £60 per ton is used.

Table 4.18 Recovery of sodium sulphate by crystallisation 1)

	Cost *(£000)*	**Cost per ton of sulphate** *(£/ton)*
Capital cost	8 000	-
Operating cost	1 000	118
By-product credit	510	60
Annualised cost	1 790	210

Note 1) Basis: 27.5m^3/hr
55g/litre sodium sulphate

This example is included to indicated the significant magnitude of this cost on a moderate-sized application. The costs may possibly be reduced if the steam is pre-concentrated with a membrane system, but the difference is likely to be marginal.

4.3.4 Disposal of liquid organics

Liquid or tarry organic wastes are produced as residues or by-products from several processes. Offsite disposal is not part of the authorisation for a process plant. However, on some occasions it may be appropriate for an incinerator or other destruction device to be installed on site. This is common practice in Europe and the United States for heavily chlorinated organic wastes. Part of the motivation for on-site destruction is economic: merchant incinerators generally charge a significant premium for the responsibility of treating difficult wastes. Technical reasons favouring on-site destruction include the advantages of a relatively consistent waste feed (compared to a merchant incinerator) and the possibilities of site integration.

The technologies described here are those directed at heavily chlorinated organic wastes.

Description: High temperature incineration

High temperature incineration is a standard technology for destruction of chlorinated organics. The operating conditions – including requirements for temperature, residence time, and free oxygen – are well known and are not repeated here. The incinerator would need to be fitted with gas cleaning to meet required limits on, for example, emissions of HCl.

One of the main process variants with incineration is in the method of control gas scrubbing.

Hydrogen chloride is highly soluble in water, so an aqueous scrubbing system can achieve high efficiencies. This provides the opportunity of recovering hydrochloric acid as a solution. If an anhydrous stream of HCl is required, it is possible to use an absorption – desorption system. This requires corrosion resistant material such as graphite or high alloys and is expensive. The alternative to the production of HCl in anhydrous or aqueous form is to neutralise it. Neutralising agents include caustic soda, sodium bicarbonate, and lime. A sodium alkali neutralising agent results in the formation of sodium chloride, providing a possible recycle to a chloralkali plant, depending on impurities.

Description: BPR Process

In the by-product recycle (BPR) process, developed by BASF and now licensed through EVC, the chlorinated hydrocarbon is burnt with oxygen to produce hydrogen chloride, carbon dioxide, and steam. The product gas stream, with HCl, can be returned to an oxychlorination plant for production of ethylene dichloride by reaction with ethylene and oxygen. The reaction in the BPR process is as follows:

$$C_xH_yCl + \left(x + \frac{y-1}{4}\right) O_2 \rightarrow xCO_2 + HCl + \frac{(y-1)}{2} H_2O$$

The reaction takes place at a flame temperature of around 2 000^{O}C and a pressure of 8 bar. The process is approved in Belgium, where it was first installed, for PCB destruction. The reaction is exothermic and steam can be generated.

For the process to work effectively, the hydrogen to chlorine ratio must be 1.3:1 or greater. At lower ratios, supplementary fuel is required, adding further inert gas to the by-product gas stream. Control of oxygen feed is also a key part of maximising the reaction yield.

The first BPR plant went on stream at BASF's Antwerp plant in 1979, to be followed by a second some years later.

In the process, the liquid organic wastes are first mixed, if necessary, and filtered to prevent blockage of the burner equipment. In the reactor, the liquid organics are burnt at high temperature and elevated pressure. Reaction heat is recovered as 23 bar steam with an efficiency of around 85 percent. Hot gas from the recycle reactor is quenched in aqueous HCl and cooled, against refrigeration, to remove water. The resulting by-product gas consists of approximately equal volumes of HCl and CO_2, with small quantities of nitrogen, oxygen, chloride and moisture.

The licensor's literature quotes an 85 percent chlorine recovery as HCl. This appears conservative in comparison with typical quoted performance figures, which imply a recovery as HCl of over 90 percent. The gas is recycled to oxychlorination. Inert gases such as carbon dioxide and nitrogen are undesirable in oxychlorination, but the quantities introduced are comparatively small.

If the oxychlorination plant is not on stream, the gas can be directed to a vent scrubber to absorb the HCl before discharge.

The water is taken from the system in an aqueous purge containing HCl at around 48 percent at system pressure. The purge also contained contaminants in the liquid organic feed stream, such as metals or salts. The purge is diluted and the pressure is reduced before disposal. It is claimed that this stream can be upgraded to high quality muriatic acid.

Description: Other techniques for chlorinated wastes

Catalytic hydrogenation of chlorinated hydrocarbons would produce HCl and hydrocarbons, both of which may be used beneficially on an integrated site. A process based on this approach has been developed by the technology company UOP and demonstrated on a pilot scale.

Other techniques include supercritical water oxidation (see Section 4.3.13) and electrochemical destruction. Both have the potential for very high destruction and removal efficiencies, although they operate in aqueous media. Plasma gun technology and molten metal baths are probably more directly applicable to liquid organics. All may be described as moving towards commercialisation.

Economics

Table 4.19 gives illustrative economics of destruction of chlorinated organic wastes by incineration and the BPR process. The basis is a waste stream of 6 000 tons per year of organics with 75 percent chlorine content by weight. Two cases are shown for the incinerator. In one, the HCl is recovered as low grade hydrochloric acid for external sale. The market for merchant hydrochloric acid is relatively small compared to the quantities that are manufactured in the chemical industry. A local market may not be available; the price used for hydrochloric acid is conservative for this reason. The other incinerator case assumes lime scrubbing and deposition of the scrubber residue.

Table 4.19 Cost of treatment of chlorinated organic wastes[1]

Technique	Capital Cost *(£000)*	Variable Cost (without by-products) *(£000 pa)*	By-products *(£000 pa)*	Fixed Costs *(£000 pa)*	Annualised Cost *(£000 pa)*
Incineration (HCl)	6 000	108	691	329	721
Incineration (Lime)	6 250	333	141	340	1 545
BPR	6 750	221	691	361	988

[1] *Wastes 6 000 tons per year with 75 percent chlorine*

In the BPR process, the recycled HCl is credited at the full cost of production of the chlorine content, calculated on the basis of an electrochemical unit (1.0 ton chlorine plus 1.1 ton caustic).

These plants are relatively large, so operating labour and associated overheads have been included in the estimate, unlike for most of the other abatement processes.

The economics are highly site-specific. They depend on factors such as the local hydrochloric acid market and the real value to the user of recycled chlorine.

4.3.15 Ground protection

The protection of soil and groundwater from contamination by spills or leakages is not specifically addressed in many of the IPC authorisations and applications reviewed by Chem Systems. The subject of landfill design and management is common to all types of activity, not only petrochemicals and large scale organics, and is not covered here. The topics addressed are those relating in particular to large facilities handling petroleum and petrochemical liquids.

Description

One of the areas of greatest risk is where liquids are transferred from or into mobile containers such as road tankers or rail cars. The techniques commonly employed include:

- connecting hoses with positive locking and self sealing devices
- level indication, and preferably high level alarm, plus automatic feed cut-off in the receiving vessel
- strictly enforced operating procedures to minimise risk of overfill and to ensure that any spills are dealt with properly
- paving of the loading/unloading area or otherwise rendering it impermeable, with drainage passed to a separator and/or emergency storage tank.

Apart from on-site landfills, the other main risk area is that of storage tanks. The techniques here include the following.

- Regular inspection and maintenance of storage tanks is necessary to check their mechanical integrity. This should in any case be part of normal scheduled maintenance. Visual inspections are performed frequently and water tests every few years, as dictated by regulations or engineering standards.

- Tanks should be in bunds with sufficient capacity for 110 percent of the volume of the largest tank. It may also be necessary to take into account dynamic aspects of a tank burst such as bund strength and wave overtopping. The possibility of contamination of underlying soil should be minimised by making the bund floor impermeable. Some West European plants are reported to use clay lining for this purpose. Others use concrete paving. Concrete itself is not impermeable to petroleum or petrochemical products. It should ideally be coated or be placed over a membrane system. In practice, concrete alone is accepted in some countries as sufficient protection because spills and losses should be present only for a short time before they are removed. German legislation, however, requires oil resistant paving with specially formulated and resin-coated concrete.

- As an example of economics, Chem Systems understands that the cost of lining a tank bund is typically around £10 per square metre. For two tanks at 5 000m^3 each, the cost would be of the order of £50 000.

- Regular inspection and maintenance of storage tanks is necessary to check their mechanical integrity. This should in any case be part of normal scheduled maintenance. Visual inspections are performed frequently and water tests every few years, as dictated by regulations or engineering standards.

- Leak detection can be fitted to large tanks. This can consist of example, channels in the top of the tank plinth, allowing leakage to escape and be identified.

- Storage tanks can be built with double walls. This, or equivalent protection, is mandatory for underground tanks in most countries. Tanks above ground may be required to have only double bottoms, facilitating leakage checks.

- Groundwater monitor wells are usually required only on older existing plants where there may be reason to suspect contamination. This applies also to containment techniques such as pumping out groundwater at appropriate places. This can induce a surface gradient in the groundwater, retaining floating hydrocarbons in the case of pollution, or it can change the direction and volume of the underground water flow. Deep barrier walls are also used.

- Underground piping or drainage is normally avoided. This is for reasons of fire risk as well as to minimise possibilities of contamination. Where underground piping is essential, it can be placed in a conduit.

Large plant should also provide emergency storage, such as lagoons, for firewater or large spills. This will permit treatment before discharge to water or land (see Environment Agency paper PPG 18).

The real environmental impact of any losses to ground will depend upon the local geology and hydrogeology. While measures such as those described above are usually required for new plant in industrialised countries, this does not necessarily apply to existing plant.

4.4 Summary of review of abatement techniques

4.4.1 Release limits

It is difficult to separate the concept of achievable release limits from the economic factors implicit in the BATNEEC concept, or in the judgements of BPEO. There may be intrinsic equilibrium limits to concentrations of emitted pollutants, of course, and side-effects such as volumes of scrubber liquor may present practical limits. However, it is often possible to design to very low concentrations of pollutants with the addition of further treatment stages or by other methods. When the German government at one period required zero emissions of trichloroethylene on metal degreasing plant, for example, the equipment designers complied, at a cost. The review of abatement techniques in Sections 4.2 and 4.3 is focused on removal efficiencies and, in selected cases, the implications on economics of differing characteristics of the stream to be treated.

If economic factors are taken into consideration, then the limits should perhaps be different for different technical applications. Pollutant type and untreated concentration, plus flowrate, are key factors. The limits proposed for the EU Solvents Directive, for example, varied generally between 50mg/m^3 and 100mg/m^3, expressed as carbon, for larger solvent-using installations. In printing works, different limits were set for different types of abatement, with 200mg/m^3 being allowed from carbon adsorbers compared to 50mg/m^3 from thermal oxidation. For chlorinated solvents in degreasing applications, the limit was 20mg/m^3.

Different limits to those for continuous flows may also be appropriate for occasional or fluctuating flows on any plant for economic reasons.

It may therefore assist Inspectors in the application of cost-based limits to use an economic criterion expressed as pounds sterling per ton of VOC abated. The calculation would need to be performed on a consistent basis, such as that used in this report. Possible indicators are given in Section 4.3.2 for average VOCs. The cost cut point should be higher for pollutants with a high impact, such as carcinogens, and lower for those at the least harmful end of the scale. Quantification of the appropriate variation is beyond the scope of this report.

In its discussions with producers and equipment suppliers, Chem Systems was told that UK limits on named organic pollutants, such as benzene or formaldehyde, were largely consistent with the expectations of good practice for continuous controllable vents. For general VOCs, the guidelines in UK Notes are:

- Class A: 20 mg/m^3 (at 100g/hr or over)
- Class B: 80 mg/m^3 expressed as toluene (at 2kg/hr or 5 tons/year).

In German TA Luft legislation, for comparison, there are three categories of organic, with limits at 20mg/m^3, 100mg/m^3 and 150mg/m^3. The distinction between the categories is made largely on the basis of human toxicity. More stringent limits are imposed on carcinogens. Local regulators in Germany may in any case require limits lower than those in the national legislation.

The general VOC limits in the UK are therefore reasonably stringent for process plant but not, as the Solvent Directive proposals suggest, the limits of technical performance in some applications.

4.4.2 Best Available Techniques

In the review of generic control techniques, few examples have been identified of novel processes and techniques being applied to petrochemical and large volume organic processes. The more fundamental question is the extent to which established techniques are applied in this industry sector internationally. Table 4.20 lists the generic techniques and criteria that are suggested as BAT, based on the research performed. The focus is on organic compounds as being most characteristic of these processes. Minimisation of pollution, and internal recycling, are preferred methods of abatement and these are shown on the table as general principles.

Table 4.20 Good practice: suggested techniques and principles

Type and source of pollution	Abatement technique
VOCs to air	
Storage tanks: volatile liquids	Internal or external floating roof tanks *or* fixed roof tanks to recovery or destruction Overfill prevention: level measurement and alarms, preferably auto cut-off
Transfer of volatile liquids	Vapour balance lines Bottom filling road/rail tankers Any net vapour displacement to recovery or destruction; maximum $35g/m^3$ outlet for VOCs (total)
Controllable vents	Abatement to achievable release concentrations for non-trivial quantities; with consideration of cost effectiveness?
Fugitive emissions	Leak detection and repair programme on equipment and fittings handling gases and light organics Progressive installation (to an agreed programme) of high integrity equipment on duties where VOCs of 'high' and 'medium' environmental impact (Class A) are handled
Intermittent emissions	All occasional vents (safety, maintenance etc.) ducted to storage/recycle or to destructive device such as flare
All VOC emissions	Minimisation at source by measures such as closed process systems, high selectivity processes, recycle or fuel use of purge streams
Aqueous effluents	Treatment at the process plant of effluents to a quality that may be adequately treated by conventional water treatment plant
Ground protection	Sealing of ground with impermeable layer where spills or leaks may occur e.g. tank bunds
Landwastes	Minimisation by process design or by recovery and re-use

5. REVIEW OF SELECTED PROCESSES

5.1 General

Chem Systems has chosen six processes or groups of processes which illustrate the contrast within the organic/petrochemicals area. These are:

- formaldehyde, produced by atypical processes, and often linked with downstream resin production on a medium to small scale
- polyolefin production, a cornerstone of commodity polymer business, with potential releases of relatively photochemically active olefins
- EDC/VCM/PVC, which has particular pollution concerns relating to vinyl chloride and other chlorinated organics
- adipic acid production, a complex process with particular abatement requirements for nitrous oxide emissions
- nitrobenzene/aniline, where there is an intractable aqueous waste that different producers tackle in different ways
- emulsion polymers – taking vinyl acetate ethylene (VAE) polymers as an example of a smaller scale process with batch processing.

These processes encompass small scale batch operations (emulsion polymers) through to large scale continuous operations (EDC/VCM/PVC and Polyolefins). In each area external environmental factors (i.e. pressures on the producer's clients such as formaldehyde restrictions and reduction of VOCs in paint emulsions) are also cost factors which producers need to conform to as well as internal production criteria.

Where possible major environmental expenditures and brief operating characteristics within these processes are highlighted i.e. N_2O emissions in adipic acid which has been recently installed.

5.2 Formaldehyde

5.2.1 Process Description

The only technologies currently used are based on methanol. There are two main types of process. One is based on a silver catalyst which is used to promote the dehydrogenation and partial oxidation of methanol at temperatures of 500 to 700 °C. The other type of process operates under conditions of excess air with metal oxide based catalysts at 250 to 400 °C. In recent years the metal oxide process has been the predominant selection for new producers. A typical metal oxide process is shown in Figure 5.1.

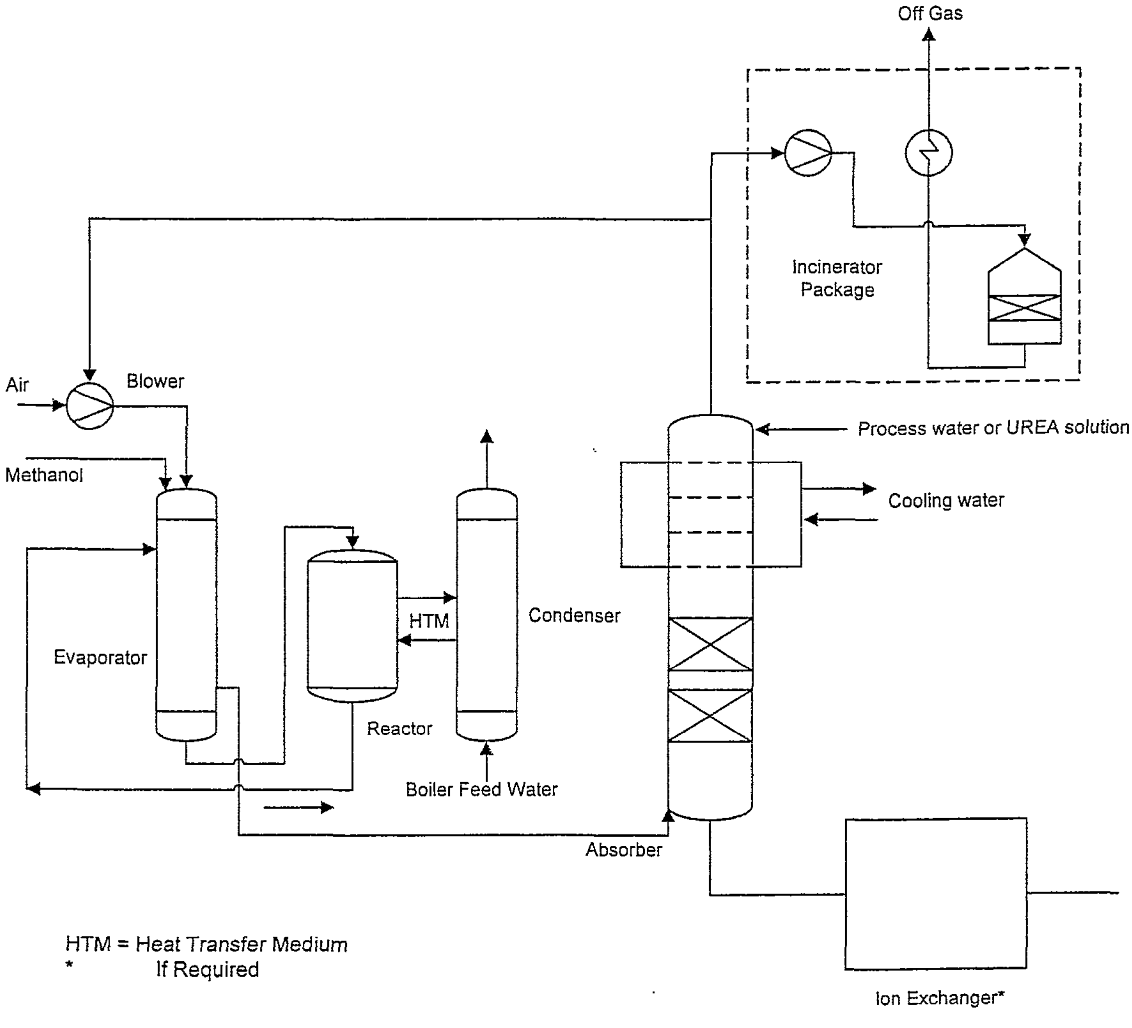


FIGURE 5.1: Formaldehyde Production: Metal Oxide Process

Methanol, air and recycle gas are mixed together and vaporised in the evaporator. The reactor feed gas is heated to around 350 °C. This mixture circulates through a condenser. Formaldehyde is condensed and absorbed to concentrations from 37 percent to 58 percent dependent on application.

5.2.2 Pollution: Sources and Methods of Control

Releases to Air

The main source of gaseous emissions from a formaldehyde plant is the tail gas.

Gas from the metal oxide process usually requires catalytic incineration. Emission limits imposed in Germany require as low as 5 mg/ Nm^3 formaldehyde which is just achievable. Other stringent limits are typically 100 mg/Nm^3 carbon monoxide and a total of 130 mg/ Nm^3 for other organic compounds such as DME, dimethyl ether. Typical operating temperatures lie in the region of 200 °C with efficiency reaching 99 percent conversion to CO_2 and H_2O using a noble metal catalyst. Other techniques used include thermal combustion and adsorption on activated carbon.

The typical results from catalytic incineration are shown in Table 5.1.

Table 5.1 Typical values of VOC component in catalytic incinerators

	IN (mg/Nm^3)	OUT (mg/Nm^3)	TA Luft (mg/Nm^3)
Dimethyl Ether (DME)	6 - 10 000	<50	<50
Methanol	1 500 - 2 000	<15	<150
Formaldehyde	150 – 700	<5	<20
CO	10 – 20 000	<100	

Running costs are very low as manpower, maintenance are usually accounted for on the formaldehyde plant. Typical catalysts are Pd/Pt wire on Al_2O_3 with a four year lifetime.

This assumption is also based on there being no requirement for excess steam (10 bar) which is produced and, in most cases, used elsewhere in the process at around 5 000 tons per year. If charged out at a conservative £6 per ton, this would yield £30 000 per year as income.

Fugitive emissions through vents of VOCs from methanol and formaldehyde storage tanks is common, as are leaks from flanges on the reactors and pipework.

Tanker offloading also releases large quantities of VOCs from the displacement of saturated air from storage and batching tanks.

The case for the silver catalyst route to formaldehyde is different to metal oxide in that excess hydrogen is produced in the offgas. This is in part due to silver catalyst plants being operated at higher methanol levels than metal oxide to avoid explosive mixtures of methanol and air. The offgas is combustible without the need for a catalytic incinerator.

Incomplete combustion of organic components can also lead to higher VOC emissions than local norms can tolerate.

Costs of abatement for a typical metal oxide formaldehyde plant are shown in Table 5.2.

Table 5.2 Costs of abatement: formaldehyde production

Technique	Capital cost *(£000)*	Operating cost *(£000 pa)*	Annualised cost *(£000 pa)*	Cost/ton of product *(£)*
Tank vent scrubbers	45	2	9	0.18
Fugitive I	8	10	11	0.22
Tail gas unit	250	13	54	1.07
Tail gas unit (steam credit)	250	(17)	24	0.47

5.3 Polyolefins: LDPE

5.3.1 Description of Process

Low Density Polyethylene (LDPE) plants have a typical capacity in the UK of around 100 000 metric tons per year.

A simplified flow diagram for LDPE including emissions is shown in Figure 5.3.

There are two conventional processes for manufacturing LDPE, tubular and autoclave. In both processes high purity ethylene is introduced into a reactor at high pressure, typically 2 000-3 000 bar and high temperature. Free radicals are initiated by the injection of oxygen or peroxides. Traces of alpha-olefin comonomer are added to give short-chained branches and hydrogen or propane are introduced to terminate the reactions. Cooling is used to keep the temperature below the 350 °C at which ethylene might decompose.

Except for the reactors, both processes are essentially the same, and are made up of five steps: ethylene compression; initiator preparation and injection; polymerisation; separation of polymer from unreacted ethylene and low molecular weight waxes; and finally extrusion and finishing (degassing, blending, storage and packaging).

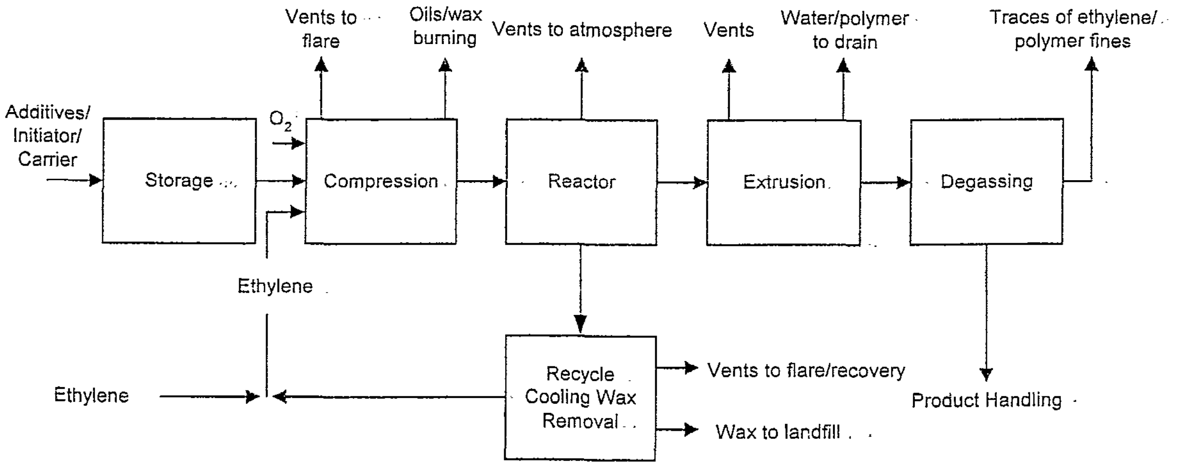


Figure 5.2 Simplified LDPE Flow Diagram

5.3.2. Sources of Pollution and Control Measures LDPE

Emissions to air

Ethylene can be lost from several sources on an LDPE plant. One characteristic of older LDPE plants is the decompression, or "decomp", when ethylene decomposes in hot spots and the reactor vents violently. The occurrence of this phenomenon can be reduced very substantially by computerised control.

The most significant other source is the purge from the ethylene recycle loop. This is necessary to prevent the build-up of inert gases. If the polyolefin plant is associated with a steam cracker on site, recycle for recovery of chemical value may be an option. Otherwise, combustion is needed, whether in fuel uses or in an abatement device.

Other sources include degassing from the polymer, with around 800 parts per million in nibs, and losses from the compressor seal system. With a high pressure gas system, other fugitive losses could be significant unless high integrity fittings are used and a Leak Detection and Repair system is adopted.

Most of the unreacted ethylene is separated from the polymer by a high pressure separator after the polymer leaves the reactor. However, a significant amount is still left in. Further degassing occurs during extrusion and can be emitted to the atmosphere. Less than 0.1 kilogram of ethylene per ton of product is emitted from this source. These emissions can be reduced 90 percent by using an underwater face cutter, which is commonly used in practice.

Pellets are purged with air for several hours to remove the last traces of ethylene and this may be emitted to atmosphere.

Aqueous effluents

Rinse water or pellet system overflow could be treated through an effluent treatment system to remove polymer fines and any organic materials.

Waste Management

A significant amount of second grade polymer is produced, but is usually sold at reduced prices. Approximately 0.1 kilogram of polymer per metric ton of product is put to waste, however. This waste polymer or waxy material comes from spills, leaking filter packs, transition material, polymer made out-of specification and decomposition resulting from equipment failure. Good housekeeping with regard to dull cutter blades or faulty thermocouples on the extruder can improve efficiency.

Costs of Control

The control techniques selected for illustrative economics relate to abatement of VOC losses. Computerised control to reduce decomp occurrence is not included as this is now a widespread technique with advantages of operational efficiency. The techniques considered are as follows:

- It is assumed that a plant will already have an existing system to collect and treat significant hydrocarbon vents such as the purge stream. An existing system may not be complete, for example on the collection of all vents from pressure relief valves. Indicative costs are shown below for collection of further vents and catalytic incineration.

- Control of fugitive emissions by a Leak Detection and Repair (LDAR) programme is the second technique. Annual inspection of components, with follow-on maintenance, is assumed.

- A more stringent level of control of fugitives is a further option, with modification of compressor seals and pump seals, plus a LDAR programme. Once more, existing plant will have at least some of this in place.

Cost estimates are shown in Table 5.3 for a 100 000 ton per year LDPE plant, operating at nameplate capacity. The costs are dependent on the exact scope, so data given are only indicative. Saved VOC is credited at a nominal £150 per ton.

Table 5.3 Low Density Polyethylene (LDPE): Summary of costs of pollution control

Technique	**Capital cost** *(£000)*	**Operating cost** *(£000 pa)*	**Annualised cost** *(£000 pa)*	**Cost/ton of product** *(£)*
Vent collection and incineration	465	108	183	1.83
LDAR	40	(3)	4	0.04
More stringent fugitives control	450	50	123	1.23

5.4 EDC/VCM/PVC

5.4.1 Process Description

A simplified block diagram is shown in Figure 5.4.

PVC is made by polymerisation of vinyl chloride monomer or VCM. There are two main routes for the production of VCM:

- from acetylene, by reaction with hydrogen chloride
- from ethylene and chlorine or hydrogen chloride, via ethylene dichloride EDC.

The acetylene route is hardly used in the West due to economic reasons. The latter route is used in Western Europe and is described below.

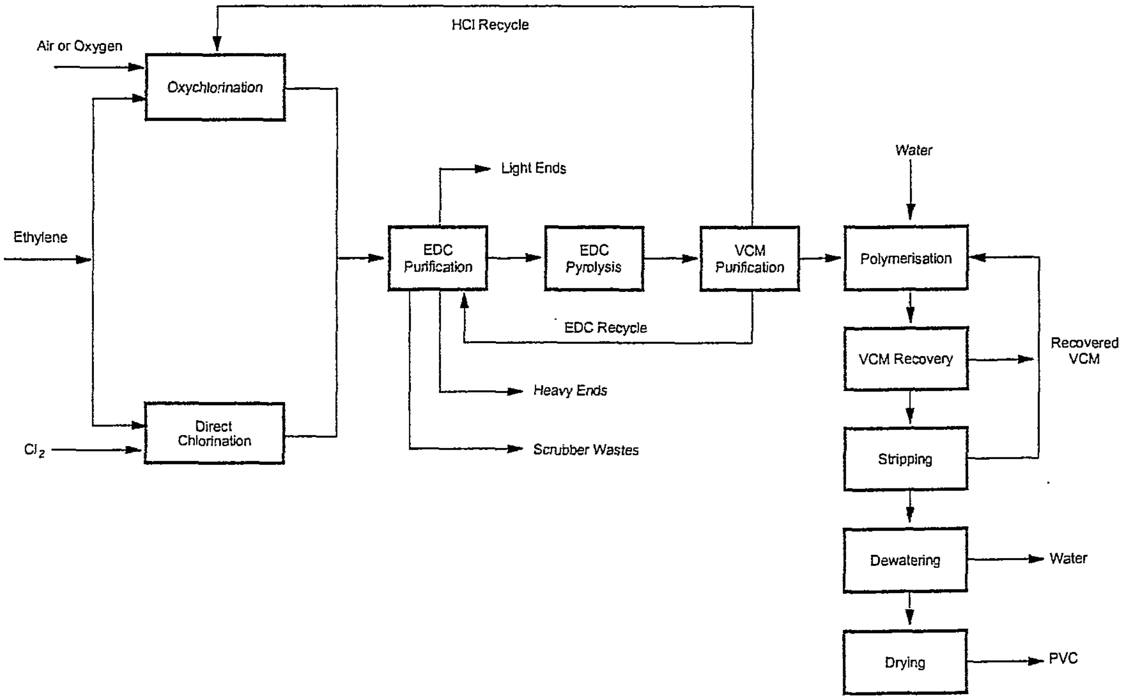


Figure 5.3 EDC/VCM/PVC production

EDC/VCM

VCM is produced by the pyrolysis of ethylene dichloride, or EDC, at 500 to 600 °C. The by-product from this reaction is hydrogen chloride. The EDC is produced either by liquid phase chlorination of ethylene, or by oxychlorination of ethylene with hydrogen chloride and oxygen. The balanced oxychlorination process uses both methods of EDC production. In this, by-product hydrogen chloride from the VCM stage is used in the oxychlorination step.

There are usually both heavy and light end by-products. The light ends contain mainly C_1 and C_2 chlorinated hydrocarbons while the heavies can contain complexes such as chlorinated cyclic or aromatic compounds. Chlorinated by-products are often used as feedstock to the production of chlorinated solvents.

PVC

PVC is made by the polymerisation of VCM. There are several process options, namely:

- suspension process
- emulsion process
- mass process.

There are other variants, such as the solution process and the gas phase process. In practice, the majority of PVC is produced by the suspension process. The emulsion process is also widely used. These two processes are described as the main options.

In the suspension process, the VCM is dispersed as liquid droplets in water by vigorous stirring and the droplets are stabilised by a colloid. The polymerisation is started by the addition of initiators and heat, after which cooling is required. Polymer tends to build up in the reactor. The closed reactor systems involve the use of organic solvents and water or steam guns. Reactor sizes have increased over the years from around 7.5 m^3 to 200 m^3. This reduces the risk of VCM leakage as well as improving productivity.

After batch polymerisation, the PVC slurry passes to the continuous section of the plant. Most of the unreacted VCM flashes off as the pressure is reduced, and is recovered. The VCM content in the final PVC is strictly limited in most markets. For this reason most plants have installed a steam stripper which removes VCM from the slurry under vacuum. The slurry is then dewatered and the PVC is dried in a drum or fluid bed dryer.

In the emulsion process, the VCM is emulsified in water which contains soaps. As with the suspension process, polymerisation is usually performed batchwise. Some plants in Germany operate continuously, however.

The batch emulsion process is similar to the suspension process. Instead of a colloid in the reaction recipe, a surfactant is used. The chemical initiator is also different. Surfactant is added as the polymerisation proceeds to aid the growth of the particles of uniform size. Large and unsaleable lumps can form, however.

Steam stripping of the reactor latex can be difficult. There are other techniques available, such as stripping in the reactor or rapid steam injection and depressurisation. Drying of emulsion PVC is normally performed in spray dryers.

5.4.2 Sources of Pollution and Abatement Techniques

a) EDC/VCM

Emissions to air

VCM is a source of particular concern as it is a carcinogen. Other gaseous pollutants include EDC and chlorinated hydrocarbons such as carbon tetrachloride. Methods of controlling losses to atmosphere include the following:

- From the EDC/VCM plant, there will be a number of vents from process and storage. Good practice is to collect all vents for incineration; a purpose built high temperature incinerator unit is desirable. Achievable levels from point sources are quoted as 1mg/m^3 for EDC and VCM combined, 0.1ng/m^3 for dioxin (TEQ) and 10 mg/m^3 for HCl.

- High integrity mechanical equipment is used to reduce fugitive emissions. This includes double seals on rotating shafts or, where available at required duties, canned or magnetic drive units. Valves require bellow seals or similar, and flanges need high quality gaskets.

- Rupture discs are used in combination with safety valves; valve vents may pass to the vents incinerator.

- Closed sewers are used to minimise losses of contaminants to atmosphere.

Aqueous effluents

Aqueous effluents may contain the following pollutants.

- VCM, EDC or other volatile chlorinated hydrocarbons may be stripped to under 1 mg/litre (total chlorinated hydrocarbons) by air or steam, and returned to the process.

- Copper catalyst may be carried out from the oxychlorination process, particularly from fluid bed catalyst units. This is of significance for dioxin emissions to water as dioxins and related substances have a strong affinity to particles. The copper can be partly removed by alkaline precipitation at pH 11-12, and electrolysis is also reported if effluents contain ammonia. Treated effluent limits of under 1 mg/litre are reported.

- The effluent can contain non-volatile chlorinated material such as chloral or chloroethanol. With alkaline treatment, these compounds can be converted to compounds that can be stripped, such as chloroform, and degradable material such as ethylene glycol.

Land wastes

By-product and waste chlorinated hydrocarbons are generated in EDC purification. Most plants are integrated to permit use of some of these streams for the production of other materials such as chlorinated solvents. The balance for companies and sites has tended to shift in recent years because of changes arising from the Montreal Protocol on ozone depletors.

Some chlorinated wastes generally require disposal, however. High temperature incineration at appropriate conditions is recognised as an acceptable technique in many countries. Where possible, by-product hydrochloric acid can be sold to offset the cost. Recovery of anhydrous HCl for use in oxychlorination is costly and requires expensive materials of construction in an absorption-desorption unit. If there is no local market for hydrochloric acid, neutralisation and disposal of reaction product would be needed.

b) PVC

The techniques mentioned below refer mostly to suspension PVC. Where comments relate to emulsion PVC, this is noted.

Emissions to air

The main issue of concern is VCM, which is of relevance for occupational health reasons as well as environmental impact.

- VCM losses from the reactors occur on opening. Best design practice incorporates anti-fouling agents which lengthen production runs. Modern reactors can also be fitted with internal spray systems to permit descaling without opening. For older plants, displacement of the gas in the reactor to a gasholder by adding water before opening is an alternative. Inert flushing systems are used when it is required to open the reactors or other equipment.

- Losses in the VCM recovery system, at the condenser vent, will be minimised if ingress of inerts is prevented.

- Apart from the VCM recovery vent, other vents include that of the inerts flush, overheads from any effluent stripper, and tank vents. Significant quantities of VCM in vent gases in general may be recovered by different techniques. Carbon absorption is one possibility, and a solvent absorption-desorption system is also feasible. As well as solvents such as Methyl Ethyl Ketone (MEK), it is possible to use EDC as a solvent. A membrane system is described in Section 4 as another option.

- All VCM in the slurry leaving the recovery vessel will leave the plant directly to the environment or in the PVC product. It is difficult to drive off the VCM in the PVC product using a drier. Removal of the VCM from the drier vent gas is also difficult. The emphasis is therefore on removing VCM adequately in a steam stripper. In the emulsion PVC process, the latex may be stripped in the reactor batchwise or in a separate vessel either batchwise or continuously.

- Fugitive emissions are controlled with high integrity equipment and fittings as on the EDC/VCM process.

- PVC dust from the driers is another atmospheric emission associated with these plants. Some plants use cyclones for dedusting the dryer vent. Installation of fabric filters is effective and relatively inexpensive.

Aqueous Effluents

- Water used in the reaction is separated from the PVC slurry after stripping. Other sources include steam condensate, washwater and seal water. This water typically contains several parts per million of VCM. A steam or air stripper is often used to reduce the chlorinated organics in the aqueous effluent. The stripped material may be sent for incineration or other treatment. The VCM in the water can be reduced to under 1 mg/litre. It is arguable that a higher limit should apply to stand-alone emulsion PVC plants, because fine particles in the effluent tend to block stripping equipment.

- PVC in the wastewater can be removed by conventional wastewater treatment.

Landwastes

Off-specification product and other solids are usually sent to appropriate landfill. Wastewater treatment sludge may be incinerated. Solids from emulsion PVC plants may contain VCM at over 1 000 mg VCM per kg PVC. This needs to be stripped or disposed of as hazardous waste, preferably incinerated to avoid VCM loss to atmosphere.

c) International legislation

EC Directive 90/415/EEC covers the manufacture and use of 1,2 dichloroethane (DCE) and is relevant to releases to water from the production of vinyl chloride monomer (VCM). In this report, DCE is termed EDC, or ethylene dichloride, which is the more usual industry designation.

The Oslo and Paris Commission (OSPARCOM) has issued draft recommendations on BAT for the manufacture of VCM (96/2) and suspension polyvinylchloride (PVC) (96/3). A recommendation on BAT for emulsion PVC is being developed.

d) Voluntary action

Industry associations are active in almost all European countries in organising voluntary action to respond to environmental concerns. Amongst these is the ECVM, the European Council of Vinyl Manufacturers. Typical figures recommended by ECVM for environmental standards are shown in Table 5.4.

Table 5.4 ECVM environmental standards

EDC/VCM		
Limits on vent gases:		
VCM	mg/Nm^3	5
EDC	mg/Nm^3	5
HCl/Cl$_2$	mg/Nm^3	30÷5
Ethylene	mg/Nm^3	150
Dioxin-like components	ngTEQ$^{(1)}$/m^3	0.1
Aqueous effluents:		
EDC	g/ton$^{(2)}$	2.5
Copper	g/ton$^{(3)}$	0.5 (soluble) 2.0 (total)
Dioxin-like components	µgTEQ$^{(1)}$/ton$^{(2)}$	1
PVC (Suspension)		
VCM emissions: production	kg/ton	0.1
VCM in aqueous effluent	mg/litre	1
VCM in regular product	g/ton PVC$^{(4)}$	5
	g/ton PVC$^{(5)}$	1

(1) Expressed as toxic equivalents
(2) EDC purification capacity
(3) Oxychlorination capacity
(4) General purpose
(5) Food/medical

5.4.3 Economics

Indicative costs of key abatement measures are shown in Section 6.5, in which the economics of the industry are reviewed.

5.5 Adipic Acid

5.5.1 Process Description

A simplified block diagram of the adipic acid process is shown in Figure 5.5.

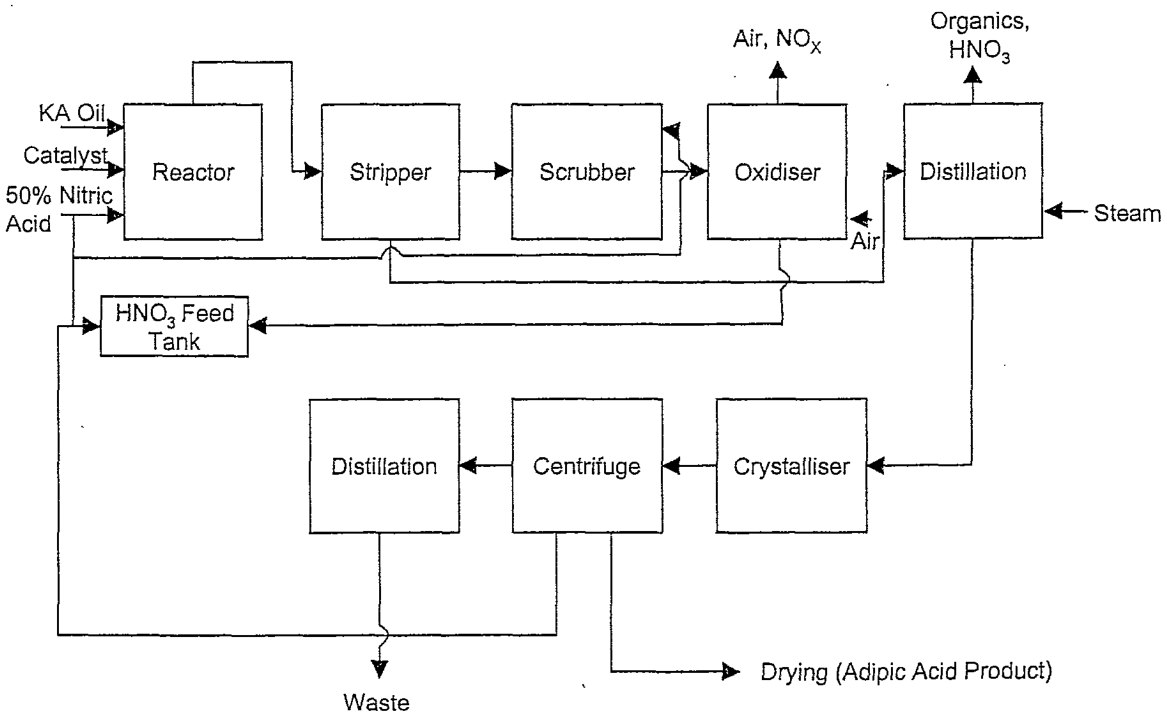


Figure 5.4 Simplified Nitric Acid Oxidation of KA Oil to Adipic Acid

Crude cyclohexanone is made by air oxidation of cyclohexane in the presence of a cobalt catalyst, at about 165 °C and 10 bar. Metaboric acid is added at about 20 percent by weight of the cyclohexane.

Nitric acid at 40 to 50 percent is used as the oxidant. Typical feed of nitric acid (100 percent) is around three times stoichiometric to the KA oil (a mixture of cyclohexanone, the ketone or K component, and cyclohexanol, the alcohol or A component). The catalyst is ammonium metavanadate and copper. Based on cyclohexane a yield of 70 percent adipic acid is obtained.

Reactor liquid product is air stripped to remove nitrous oxide. It is then steam distilled to remove unreacted nitric acid and low boiling organics (as overheads). Liquid from the bottoms of the steam still are cooled to 40 °C.

This crystallises out the adipic acid. Crystals are separated from the mother liquor, redissolved in water, and recrystallised to remove impurities – the crystals are then dried.

Nitrous oxide is produced as a gas. This is oxidised with air, and scrubbed with water to produce nitric acid, which is recycled to the reactor. Overheads from the steam contain some nitric acid which is recovered and recycled to the reactor.

A portion of the mother liquor from the first crystallisation step, which contains nitric acid and catalyst, is recycled to the reactor. Another portion is fed to a still. Overheads from the still, containing water and nitric acid, are recycled to the reactor. The bottoms are cooled to crystallise out adipic acid, which is combined with crystals from the first step.

Mother liquor is distilled to recover nitric acid which is concentrated and recovered. Bottoms undergo additional processing to recover the catalyst.

5.5.2 Pollution: Sources and Methods of Control

Air

Emissions of nitrous oxide from adipic acid manufacture account for 5-8 percent of the anthropogenic emissions worldwide. N_2O is considered a powerful greenhouse gas with a direct global warming effect 260 times that of carbon dioxide for a 20 year time horizon.

Nitrous oxide is produced from the oxidiser in the reaction offgases after NOx recovery.

Typical adipic acid reaction offgas analysis is shown below in Table 5.5.

Table 5.5 Typical Adipic Acid Reaction Off-Gas Analysis

Component	Mol %	
N_2O	30.5	$(30 \rightarrow 50\ \%)$
NOx	0.7	
CO_2	6.0	
CO	0.03	
O_2	3.9	
H_2O	2.0	
N_2	56.84	
VOC	0.03	

The unit operations which could be considered BAT are thermal destruction, recycling or catalytic decomposition. Most of the major producers have formed an inter-industry group to share information on these technologies. Boiler abatement practices at various sites worldwide will be phased out in the medium term and replaced by the above techniques.

In spite of this collaboration it still requires several years development work on the pilot scale to optimise the process as well as catalyst performance.

One possible technique, based on catalysts, is being developed by a German producer. Typical performance parameters achieved in Europe for this technique are shown in Table 5.6.

Table 5.6. Typical performance parameters for Catalytic Decomposition of N_2O

Temperature in catalyst zone		700 – 800 °C	
Catalyst		Pd on Al_2O_3 carrier (3 year lifetime)	
Efficiency	N_2O	>98 %	removed
	NOx	>90 %	
	VOC	>98 %	
	CO	>99%	

Temperature control of the exotherm is required when N_2O is converted. Control techniques include dilution by air or direct heat removal from the bed.

Typical indicative costs for catalytic incineration of N_2O on adipic acid plants are shown in Table 5.7.

Table 5.7 Cost of reduction of nitrous oxide

Technique	**Capital cost** *(£000)*	**Operating cost** *(£000 pa)*	**Annualised cost** *(£000 pa)*	**Cost/ton of product** *(£)*
Catalytic incineration	3 500	50	619	3.09

Other air emissions are particulates from adipic acid from the dryer vents. Typical techniques include bag filters and water scrubbing.

Aqueous

There are two types of water pollution, inorganic and organic. The inorganic materials include the catalysts. Copper salts usually copper nitrate and vanadium salts. These can be recovered using ion exchange systems. The mother liquor from the centrifuge contains high concentrations of glutaric and succinic acids.

In some instances these are by-products and are sold commercially for such uses as acidifying agents. Typical aqueous effluent is produced at a rate of 0.3 t/t of adipic acid for the boric acid route.

Traditional recovery unit operations include evaporators and dryers. Typical effluent pH ranges are around 1 to 2 which causes problems with standard materials of construction and corresponding maintenance costs. Maintenance costs for adipic acid plant are around 5% of ISBL (Inside Battery Limits) cost and well above industry norms of 2 to 3% due to the pH and its effect on the process equipment.

Typical BOD loadings from such plants are approximately 15-20 kg BOD/ton of adipic acid (12 ton per day, 330 days per year) dependent on the commercial issues related to recovery of glutaric and succinic acids. Biological treatment is used prior to waste water treatment by either central site or local municipal facilities.

5.6 Nitrobenzene/Aniline

5.6.1 Process Description

A simplified block diagram is shown in Figure 5.6 to illustrate potential emissions within the nitrobenzene/aniline process.

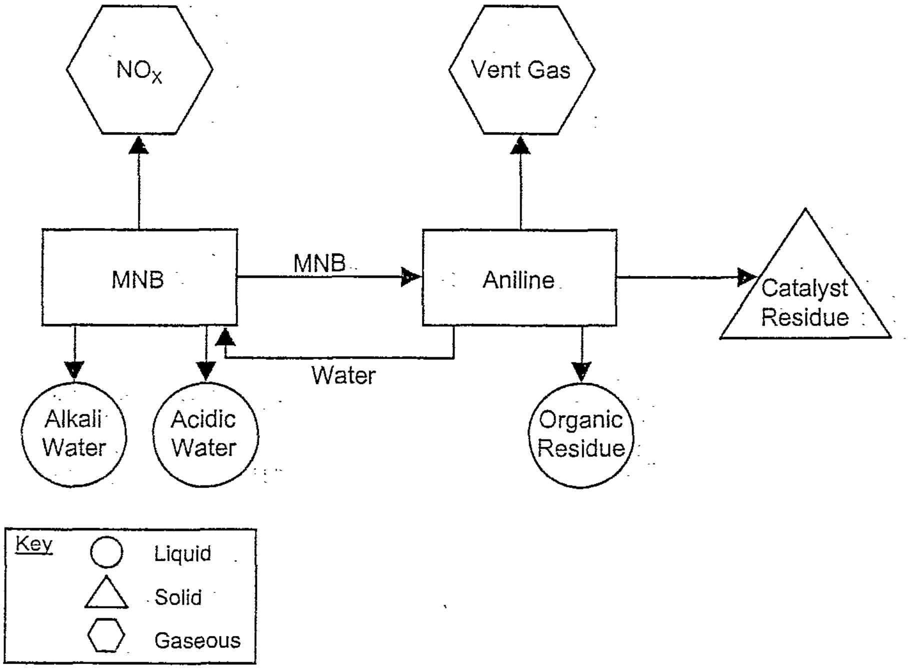


Figure 5.5. Potential emissions on simplified Nitrobenzene/Aniline process

There are a number of licensors who provide the continuous nitrobenzene technology. Aniline process is based upon vapour phase hydrogenation in a fluid bed reactor. Benzene, nitric and sulphuric acid are mixed in conventional stirred tank reactors at around 70 °C. Benzene is converted at a selectivity to nitrobenzene of 97 percent.

Nitrobenzene from the decanter is washed with dilute soda ash solution to remove entrained and dissolved acid.

In the aniline section nitrobenzene is charged with hydrogen at a molar ratio of 1:10 into a fluid bed reactor. The reaction takes place at around 270 °C and 3 bar to achieve a selectivity to aniline of 98 percent in nitrobenzene. Copper catalyst on silica is used, which needs regenerating every three months.

5.6.2 Pollution: Sources and Methods of Control

Air

- NOx emissions from nitrobenzene are often controlled by caustic scrubbing prior to discharge to atmosphere.
- Vent gases (mainly methane and hydrogen) have a high calorific value and can be sent to the site fuel gas header main according to site layout or, alternatively, are burnt.

Solids

- Catalyst residues (copper/silica) are either disposed of by landfill or recycled.

Aqueous

- Nitrobenzene has two liquid effluents: alkali water which represents a major pollutant, and acidic water. The acidic water stream is usually managed in a conventional bio-treatment plant after neutralisation.

- Alkali water (sometimes known as "red water") is particularly toxic and contains toxins such as nitrophenols and picrates. These toxins pass from the organic phase to the aqueous phase during washing. Typical concentrations range from 1 000 to 10 000mg/litre. Various abatement techniques have been employed including wet air oxidation, incineration and charcoal adsorption followed by incineration.

Wet air oxidation

Wet air oxidation offers a relatively low cost solution for destruction of intractable organics in water. The alkali water is pumped to 100 bar and 300 °C with or without air. The toxins cleave to carbon dioxide and the low molecular weight organics. Treated water contains traces of organics and can be disposed of in conventional bio-treatment plants.

Typical results obtained by wet air oxidation for nitroaromatic substances which have a very poor bio-degradability are:

COD/BOD_5	Ratio inlet	10
COD/BOD_5	Ratio outlet	2

Effluent with a COD/BOD_5 ratio of 2.5 is normally suitable for bio-treatment. COD elimination is normally 70 to 90 percent dependent on site specifics.

Typical operating costs for wet air oxidation are shown in Table 5.8.

No manpower costs are assumed as the process is regarded as fully integrated. Maintenance costs are high due to the acidic pH range and consequent choice of resistant materials such as titanium or alloy.

The variable cost element is dependent on whether fuel is internally generated. Volumes of red water vary, dependent on the waste minimisation procedure adopted on site and can be as low as 0.15t/t of nitrobenzene.

Adsorption/incineration

Some companies have adopted adsorption/incineration which incorporates adsorption of the organic compounds on charcoal or absorption into methanol followed by solvent stripping. Typical costs for this technique are illustrated in Table 5.8.

Table 5.8 Typical costs for abatement techniques, Aniline/Nitrobenzene

Technique	Capital cost *(£000)*	Operating cost *(£000 pa)*	Annualised cost *(£000 pa)*	Cost/ton of red water *(£)*
Wet air oxidation	4 000	225	875	17.50
Adsorption/ incineration	3 000	375	862	17.24

Occasionally incinerators are shared with other facilities due to the low volumes of material to be processed.

The treated water passes through biotreatment facilities as with other techniques.

5.7 Emulsion Polymers

5.7.1 Process Description

There are many types of polymer and latex which can be defined under the general category, emulsion polymers. These include acrylic and vinyls which are batch multi-purpose plants, and pressure polymers such as VAE (Vinyl Acetate Ethylene) and SB/SBR Latex, which are single purpose plants.

The VAE process is described here.

The VAE process is shown in simplified form in Figure 5.7. VAM (Vinyl Acetate Monomer) is unloaded from a rail car to a floating head storage tank and pumped to the reactor. Ethylene is pressured and vaporised. The reactor is up to 30 m^3 capacity operating at 100 atmospheres to yield a VAE copolymer of 40 to 50 percent ethylene content. Reaction temperature is between 40 and 75 °C. When unreacted VAM is between five and 20 percent by weight the emulsion is removed and sent to the post polymerisation reactor.

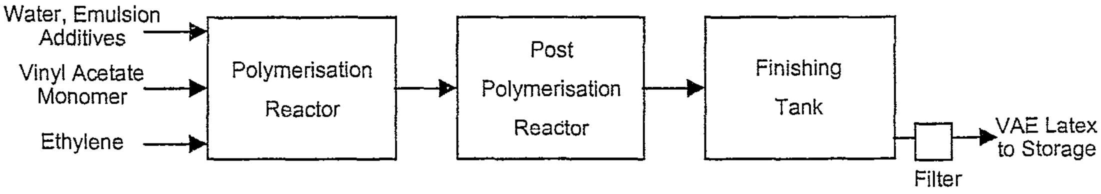


Figure 5.6. Simplified Vinyl Acetate Ethylene Latex production process

Ethylene is flashed from the reactor to the post polymerisation reactor. Total reaction times range from five to ten hours. Unreacted VAM is polymerised to a level below 0.5 percent. The product emulsion is steam stripped if unreacted monomer level is above this level.

The emulsion is cooled and sent to a finishing tank where it is filtered and pumped to storage for sale as a solution at approximately 50 percent weight solids or to spray drying for redispersible powders.

Polymer wastage is of the order of two to five percent in the process.

5.7.2 Pollution: Sources and Methods of Control

Air

- VOCs from storage tanks and process vessels are removed from the emission source via gas scrubbing. Good targets for control purposes are less than 350mg/m^3 VAM. Good practice is minimal numbers of flanges with a mass spectometer to measure fugitive emissions around pumps, flanges and storage tanks. If VCM (Vinyl Chloride Monomer) is used precautions on the level of emission of around 5 mg/m^3 prior to plant shutdown is practised in Europe.

- Unreacted ethylene, usually around two percent of feed along with organics are burned in a waste flare.

Water

- Waste water from vessel/equipment clean out is recycled.
- Water from spillages is often flocculated to ten percent by weight solids which is in turn suitable for landfill as an inert solid. Biological treatment caters for the liquid phase.

Solids

- Offgrade polymer is reworked into secondary grade product or disposed of with other solids (normal wastage is around three percent of polymer)

Pollution abatement techniques

- VOCs, ethylene and other organics have been reduced by incineration.

Typical costs for a 20 000 tons per year VAE plant are:

	Annual cost
Capital cost	£1 million
Running cost	£160 000

This equates to around £16.10 per ton of VAE produced assuming a 16.25 percent annualised capital charge, as previously mentioned.

Typical performance characteristics of such incinerators are:

Temperature	750 to 1 000 °C
Efficiency	98 percent on VOCs
Very low levels of dioxins	0.003ng TEQ/m^3

Economics

- Incineration of waste polymer (as an inert material and at one percent of polymer usage) is estimated to cost approximately £500 per ton on a 20 000 tons per year VAE plant. Total annual running costs are estimated at around £100 000 per year for such a plant.

- Fugitive releases: typical good practice includes centrifugal or sliding vane pumps with mechanical seals. Determination of leaks is carried out by measurement at flanges, pumps and VAM storage tanks as with other processes when preventing VOC emissions.

6. Review of Economic Factors

6.1 General

The purpose of this part of the report is to put the cost of pollution abatement into the context of the economics of the industry. This will assist Inspectors in assessing whether abatement measures constitute BATNEEC.

6.1.1 Process cases

The processes covered are not part of a homogenous industry, and the economic factors vary widely. Six cases have been analysed that are either representative of a number of processes or are single processes of interest.

The six process cases are:

- **Basic petrochemicals**, representative of large scale processes producing basic petrochemical building block products.
- **Formaldehyde**, a production process with distinct variants, often integrated with small downstream operations.
- **Polyolefins**, including the various forms of polythylene and polypropylene, illustrative of commodity polymers where production technology is developing rapidly.
- **EDC/VCM/PVC**, a chain of production processes resulting in production of a commodity polymer – PVC – but with specific environmental issues and solutions.
- **Emulsion polymers**, representative of medium-sized process plant (although often owned by big companies).
- **Nitrobenzene/aniline**, a process with specific pollution issues that require relatively costly solutions.

For each of these, a brief description is given of the industry sector, the cost of abating pollution, and the financial impact in the context of industry economics.

6.1.2 Basis of economic analysis

Pollution abatement measures, particularly those involving minimisation of pollution at source or beneficial recycling, may be introduced in some circumstances at zero cost, or even bring net financial credit. Often, however, there is a net cost to pollution abatement. The economic analysis in this section is intended to relate the cost of pollution abatement to profitability of the company. There are several elements to be considered.

- The price of the product in the marketplace may be set by several mechanisms, including the cost of production of competing producers, or the value to the user.

- The cost of supplying the product to the market includes the cost of production, handling and marketing costs and freight. A producer with a strong location advantage may be able to pass on costs to consumers.

- Cash cost of production is often used as a marker in assessing the economic characteristics of chemical production processes. This reflects the fact that many plants are old enough to have been written down in the financial accounts, so that capital charges are not an essential part of the analysis. However, product prices are nonetheless generally sufficient to permit reinvestment by the most economically competitive producers, unless the total demand for the product is static or declining.

- Investment in pollution abatement is, in the context of IPC Guidance Notes, new investment. It is therefore appropriate to include a capital charge in assessing the annual cost of new pollution abatement investment.

6.2 Basic petrochemicals

6.2.1 Industry characteristics

The first of the process cases considered in the economic analysis is basic petrochemicals. Processes falling into this category include most of those under Section 4.1 of the Regulations (SF 1991 No. 472). In addition, several of the major monomers, such as styrene, have the characteristics of this group.

Table 6.1 indicates some processes in this category and the number of plants. Almost all of the plants fall into the category of being large on the criterion of turnover. The operators are large chemical companies or petroleum companies. Many of the plants are relatively old, but most have been periodically revamped in the course of expansions.

Petrochemical processes are based on petroleum feedstocks such as naphtha gas oil, or associated gas. Petrochemical building blocks such as olefins and BTX aromatics (benzene, toluene and xylenes) are converted in downstream processes to other petrochemicals. Final chemical products of the petrochemical industry include polymer resins for processing into plastic products, solvents and surfactants. The 'basic petrochemical' processes reviewed here are typically those in the first or second stage of a petrochemical processing chain. The products are usually commodity intermediates that are supplied to other chemical plants or companies.

Basic petrochemical products are sold on chemical specifications rather than (usually) brand name or performance in use. As a result, competition is focused heavily on price. Within any region, such as Western Europe, different producers have differing costs of production. The differences arise from, for example, variations in scale, in feedstock source and type, and in process plant. The price for a product is related to the cost of production of the incremental source of supply, at the more expensive end of the cost curve. This is described more fully in Section 6.2.2. In essence, the basic petrochemical business is characterised by competition on price with cost of production playing a very large part.

The commodity petrochemical business is highly cyclical. This corresponds to some extent to normal business cycles in demand. It is accentuated by the large scale nature of the fixed investment, and the understandable tendency for producers to plan new capacity when cash flow is good. With the long lead times of projects, the result is frequently over-capacity, depressing margins dramatically (see Section 6.2.2).

Table 6.1 Basic petrochemical manufacture in the UK (illustrative processes)

Process	**Company**	**Capacity** *(thousand ton per year)*	**Year of Start-Up**	**Last Extension**	**Ownership Pattern/ Other Information**
Butadiene	BP, Grangemouth	60	Pre-1976	1995	-
	BP/ICI Wilton	100	Pre-1976	-	-
Ethylene	BP, Grangemouth	420	1993	1996	Ethane/Propane/ Butane Feed
	BP, Grangemouth	280	Pre-1976	Planned 1998 (+40)	Naptha/LPG Feed
	Exxon, Fawley	100	Pre-1976	-	-
	Exxon/Shell, Mosmorran	680	1985	Planned 1998 (+120)	-
	ICI/BP Wilton	865	1979	1997	-
Ethylene oxide and ethylene glycol	Union Carbide, Wilton	300/200	Pre-1976	1997	Formerly ICI. Became UCC owned in 1995
Acrylonitrile	BASF, Seal Sands	280	Pre-1976	1997	Increase in capacity due to debottlenecking
Styrene	BP, Baglan Bay	140	Pre-1976	-	One train closed in 1994, halving capacity
	Enichem, Hythe	60	1990	1991	

Two further features of this industrial sector are relevant. Firstly, producers may be integrated upstream – in preceding processing steps or in refining – or integrated downstream, perhaps to final product manufacture. Integration can improve the cost competitive position of companies. Secondly, competition is on a regional or even a global basis. Regions with low feedstock costs, primarily the Middle East, may produce basic petrochemicals and export to Western Europe. Table 6.2 shows the net trade for the UK for selected products. Care is therefore needed in assuming that the impact of additional costs will be the same for every company producing a certain basic petrochemical.

Table 6.2 Net UK Export/(Import) for selected petrochemicals

		1993	1994	1995	1996[1]
Styrene	*(000 ton)*	(35)	(164)	(177)	(205)
	(% consumption)	(11)	(45)	(48)	(55)
Ethylene Oxide	*(000 ton)*	-	(8)	(23)	(46)
	(% consumption)	-	(3)	(9)	(24)
Ethylene Glycol	*(000 ton)*	(81)	(85)	(83)	(85)
	(% consumption)	(66)	(65)	(63)	(60)
Acrilonitrile	*(000 ton)*	(5)	(7)	5	10
	(% consumption)	(2)	(3)	2	4

(1) Estimate

6.2.2 Industry economics

The analysis in this section is derived from Chem Systems' annual subscription programme, Petroleum and Petrochemical Economics (PPE). This programme includes monitoring and analysis of industry profitability for commodity petrochemicals and polymers. Chem Systems defines a Leader and a Laggard plant for each product. These represent, broadly, the best 20 percent and the worst 20 percent respectively of the regional cost curve.

a) *Cyclicality*

The cyclical nature of the business is illustrated on Figure 6.1. This is calculated on the basis of margins for Leader plants producing a weighted basket of commodity petrochemicals and polymers. For less competitive plants than Leaders, the cash cost margin may well be negative in the troughs in the business cycle.

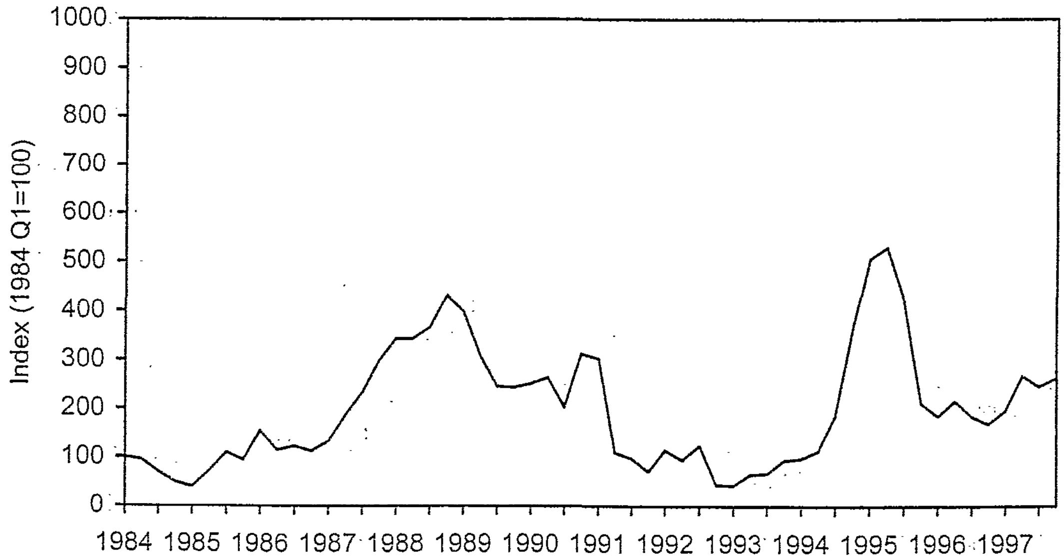


Figure 6.1 Profitability of West European petrochemical and polymer industry

b) Cash cost of production

The cash cost of production in any process includes variable costs, which are largely dependent on throughput, and mainly fixed costs such as operating labour, maintenance costs, and site overheads. To the cash cost ex-works must be added costs of freight to purchaser and of technical service and sales. The cash costs, as calculated by Chem Systems, exclude costs of corporate administration and any element of capital charge, such as depreciation, financing cost, or return on investment.

The cash costs for a number of selected products are shown in Table 6.3 for West European leader plants in 1997. Total capital is the replacement cost of the plant. The cost of feedstock is a dominant element in the cash costs of most commodity petrochemicals, accounting for most of the variable cost. The costs are indicative of North-West Europe, rather than exactly representative of UK plants. The costs will fluctuate significantly with the price of feedstock.

Table 6.3 Cash costs of production for selected basic petrochemicals, West European Leader plants, 1997 prices

		Butadiene	**Ethylene**	**Ethylene Oxide**	**Ethylene Glycol**	**ACN**	**Styrene**
Capacity	kt/a	90	620	225	186	200	460
Total Capital	£ million	45	393	107	93	136	173
Net Variable Costs[1]	£/t	146	107	329	252	388	269
Total Fixed Costs	£/t	27	30	29	36	44	20
CASH COST	**£/t**	**173**	**137**	**358**	**288**	**432**	**289**
Freight	£/t	24	12	25	21	29	14

(1) Net Variable Costs include credit for by-products

c) Profitability

In addition to the costs of production, a key parameter is the margin or profit element. The cost curve for the total industry in which a plant competes is an important determinant. The price in a commodity business will be set by plants at the least economically competitive end of the cost curve. The steepness of the cash cost curve is an indicator of the potential for a competitive producer to make profit.

Figure 6.2 shows a cash cost curve for ethylene in Western Europe. The shape of the curve represents not only differences in efficiency and scale of plants, but also different feedstock sources.

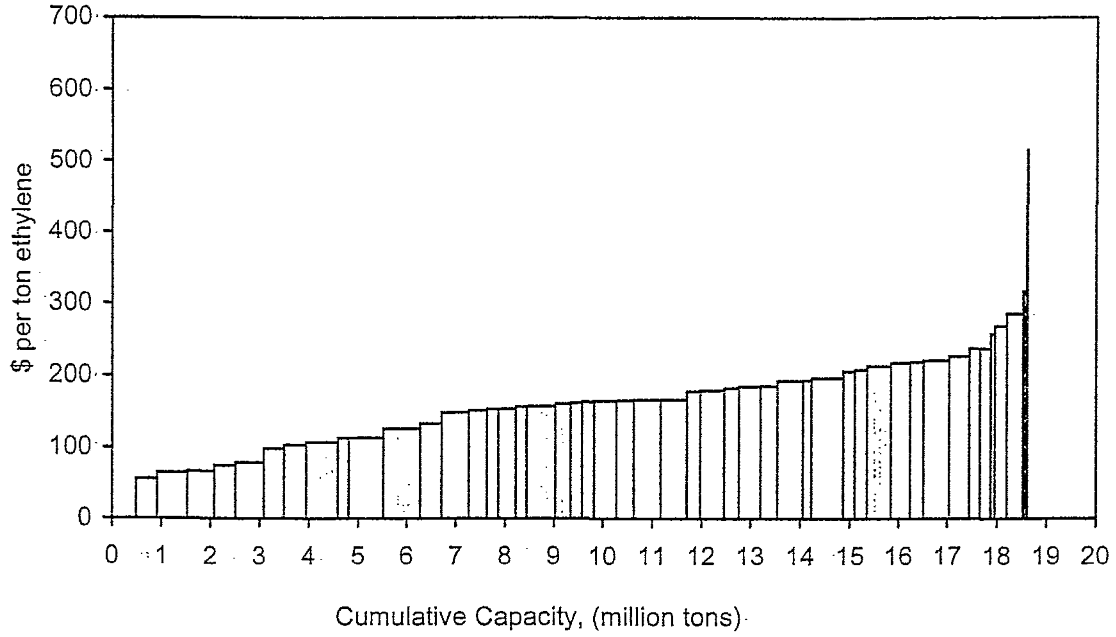


Figure 6.2 **Cash cost curve for ethylene, Western Europe**

A simple indicator of the steepness of the cash cost curve is the difference between the cash costs of Leader and Laggard plants. This is presented in Table 6.4.

Table 6.4 **Difference between Leader and Laggard cash costs for selected petrochemicals, Western Europe, 1997 Prices**

Petrochemical	Leader £/ton	Laggard £/ton	Difference £/ton
Ethylene	137	198	61
Ethylene Oxide	358	415	57
Ethylene Glycol	288	378	90
ACN	432	510	78
Styrene	289	326	37

Cash cost margin histories for the example petrochemicals are shown on Figures 6.3 to 6.8 for West European Leader plants. The margins fluctuate widely, largely synchronised with the industry business cycle. This indicates that changes in costs cannot be passed on to consumers. Both buyers and sellers are well informed in these markets and will press for the benefits of over-supply or under-supply respectively.

Other conclusions to be drawn from this analysis are:

- at some times in the business cycle, companies may suffer a cash shortage or deficit
- it is not meaningful to quote environmental costs as a percentage of margin for a single year; averaging across the business cycle is needed
- commodity producers cannot pass on cost increases that apply only to them

- the position of a plant on the cash cost curve determines whether it breaks even or suffers a significant cash drain in poor times. In practice, this seriously influences companies' decisions on plant closure and exit from the business.

6.2.3 Costs of abatement

It is difficult to assess the costs of abatement on a group of processes, or even on one process, because the requirements and the costs will be site-specific. To put some of the control techniques into an economic context, a simple generic case is taken as basis. This does not represent a specific process, but has several elements that occur in petrochemical facilities. The generic case is shown on Table 6.5.

Table 6.5 Generic petrochemical plant

Element	Unit	Basis
Production (liquid of moderate volatility)	ton per year	200 000
Feedstock (liquid at ambient conditions)	ton per year	100 000
Purge stream with air	m^3/hr	50 000
	g/m^3	5
Difficult aqueous stream with organics	m^3/hr	5
Main fired heater/furnace	MW	35

The illustrative abatement techniques are as follows.

- For control of losses from storage and loading, three types of techniques are considered. One is the installation of an internal floating roof on the four storage tanks. A single stage vapour recovery unit (VRU) and a second VRU stage are the other two techniques.

- Fugitive losses are taken to be controlled by Leak Detection and Repair (LDAR). Two levels are examined, as noted in Section 4.3. Level I requires annual inspection of gas and liquid components, while Level II is more stringent.

- A hydrocarbon purge in an air or inerts stream is assumed to arise from the generic process. In practice, this is not perhaps completely characteristic of most petrochemical plants, where inerts volumes are usually small. It is possible that streams with a significant organic content could find a home in the site boiler or other heaters, unless there are technical or regulatory problems with this. For the purposes of economic analysis, the abatement technique considered is that of thermal oxidation with energy recovery.

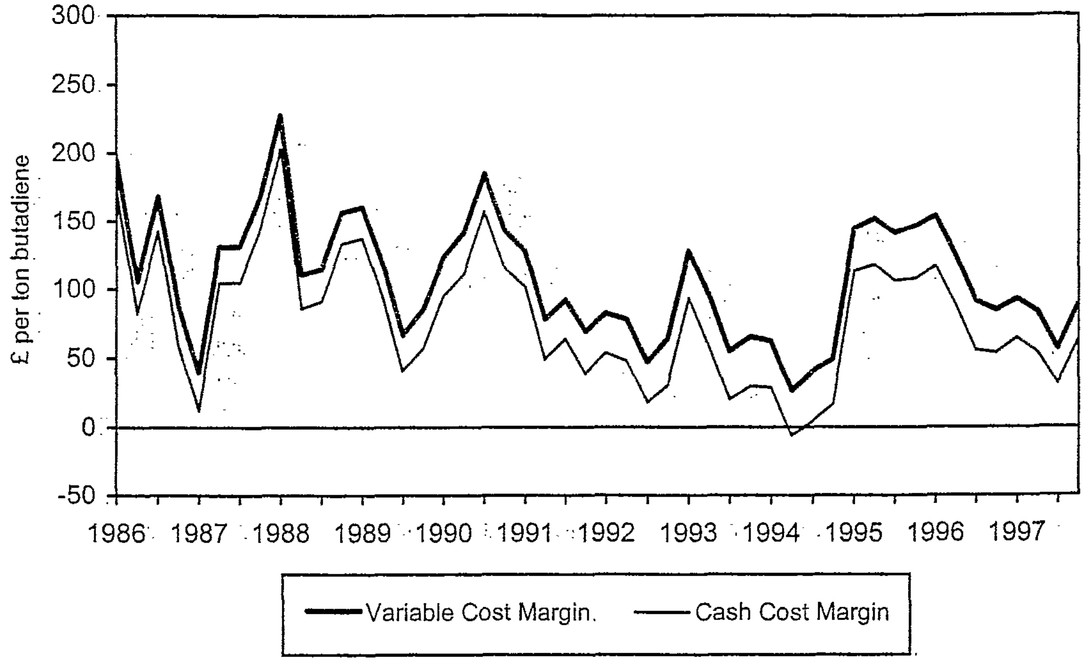


Figure 6.3 Cash cost margin for butadiene, Western Europe

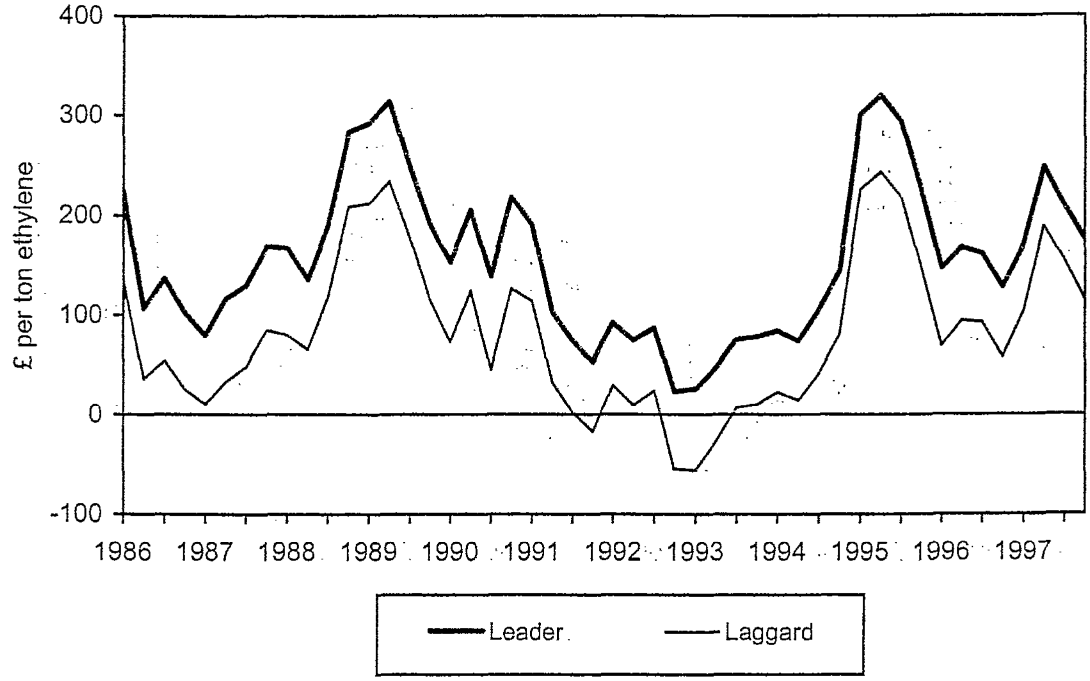


Figure 6.4 Cash cost margin for ethylene, Western Europe

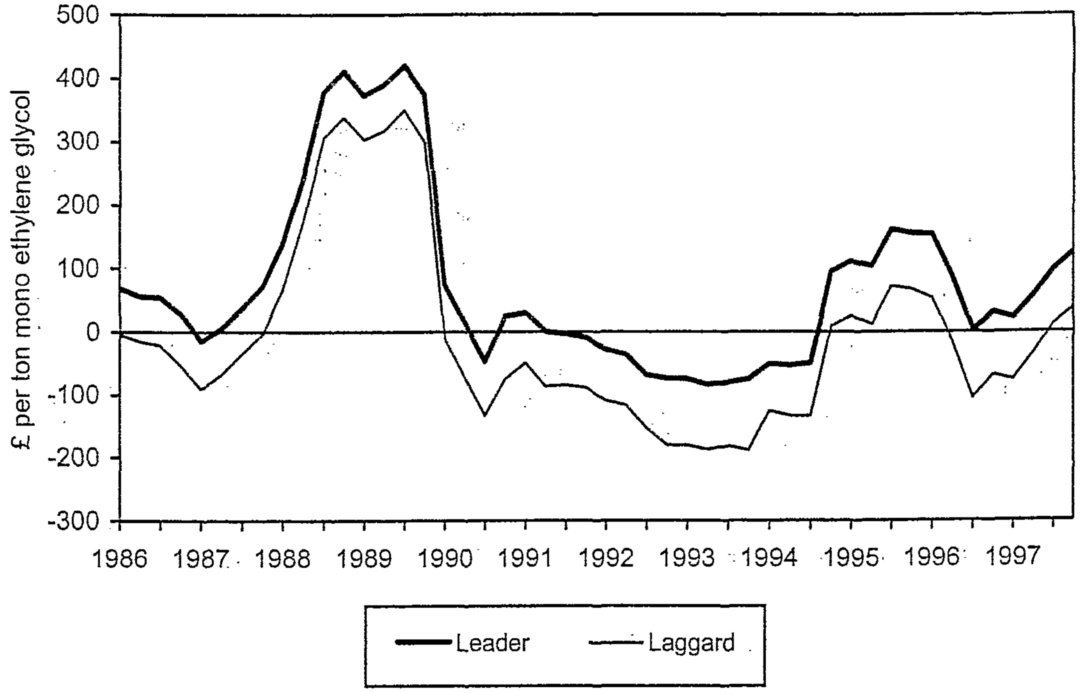


Figure 6.5 Cash cost margin for ethylene glycol, Western Europe

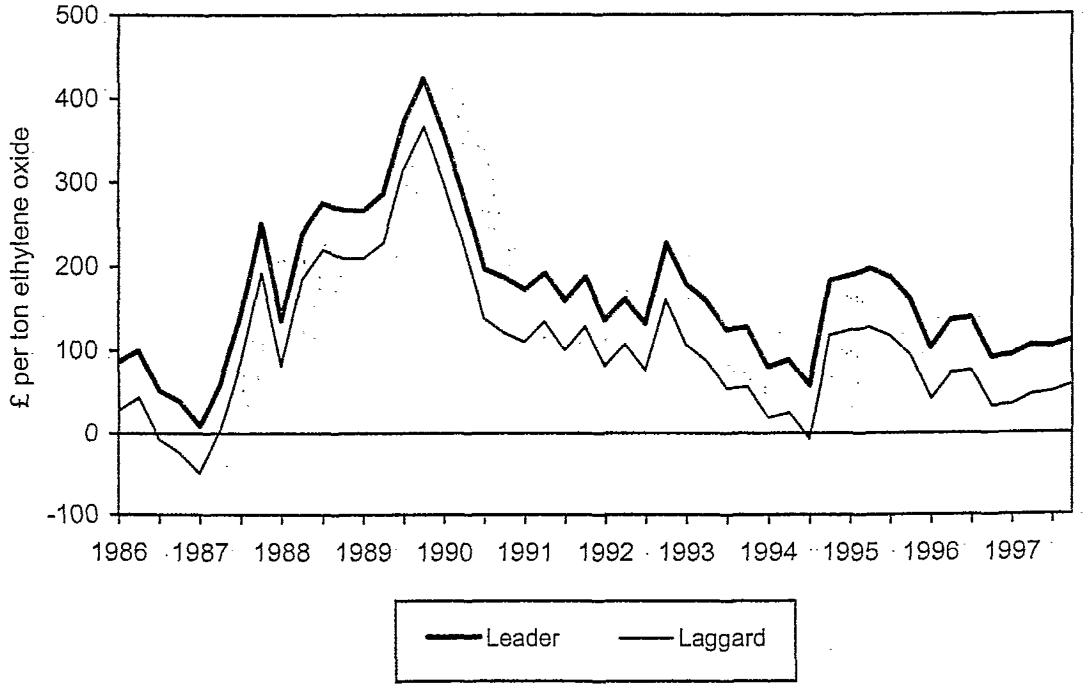


Figure 6.6 Cash cost margin for ethylene oxide, Western Europe

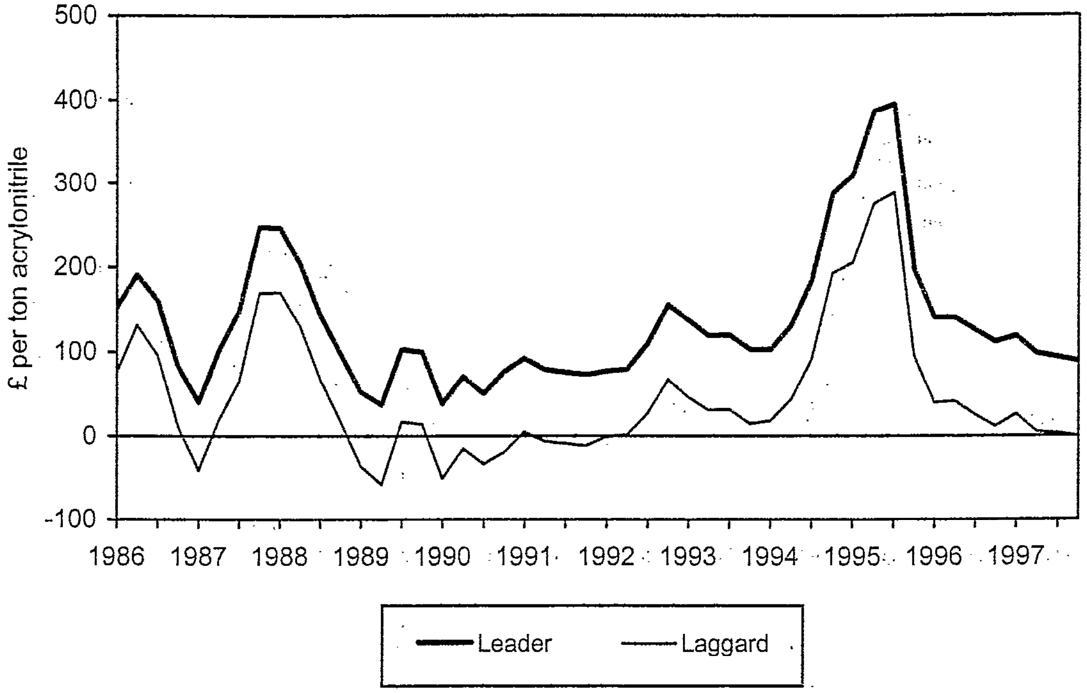


Figure 6.7 Cash cost margin for acrylonitrile, Western Europe

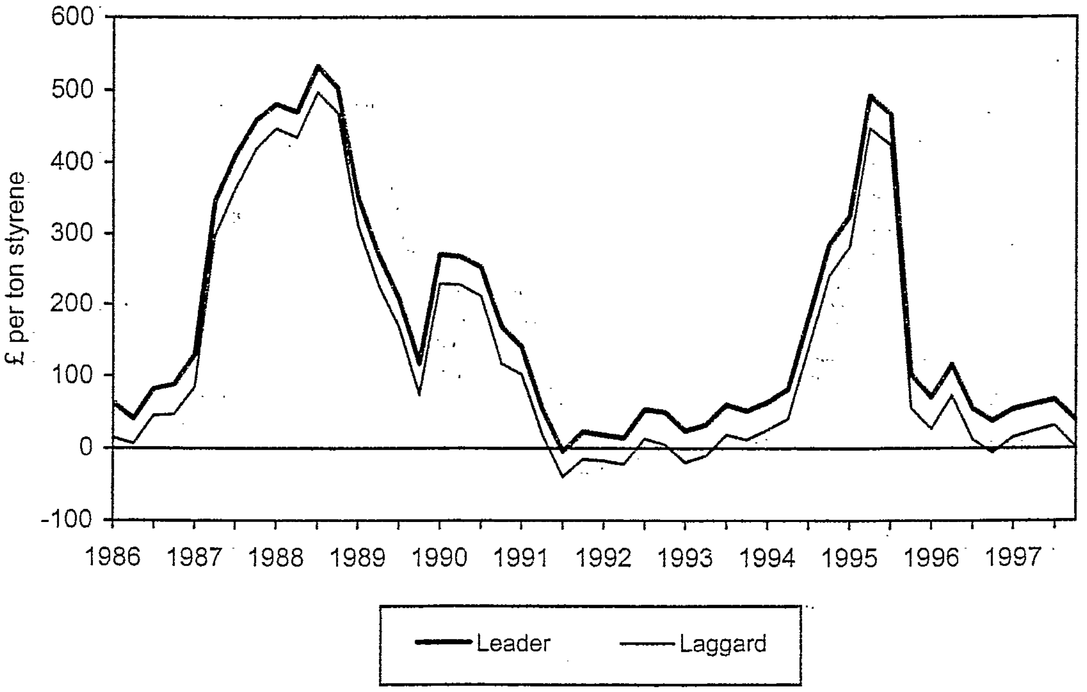


Figure 6.8 Cash cost margin for styrene, Western Europe

- Application of Selective Catalytic Reduction (SCR) to abate NOx emissions from a process furnace is an unusual requirement, although Chem Systems understands that regulators in Germany have requested it when considering a new ethylene cracker application. However, this is included as an example of rather a costly measure.

- Some processes produce relatively small volumes of difficult aqueous wastes with a significant organic content, such as from caustic scrubbing. The technique considered to abate this is wet air oxidation.

- Finally, a nominal cost is included for coating the floors of storage tank bunds with concrete that is impermeable to hydrocarbons, as an example of ground protection measures.

All these are add-on techniques rather than representing any form of fundamental redesign. It is impossible to generalise on the costs of waste minimisation and recycling.

Table 6.6 shows the costs of the selected abatement techniques on the generic petrochemical plant. The annualised costs per ton of product are also shown on Figure 6.9, with cumulative costs starting with the cheapest techniques. The techniques address different pollutants, so the x-axis is non-quantitative.

Table 6.6 Costs of abatement: generic petrochemical plant

Technique	**Capital** *£000*	**Operating cost** *£000 pa*	**Annualised cost** *£000 pa*	**Cost/ton of VOC** *£*	**Cost/ton of product** *£*
VOC					
Internal floating roof	157	-1	25	964	0.12
Loading VRU	1 000	28	190	2000	0.95
Loading VRU II[1]	160	5	31	6715	0.16
Fugitives I	40	0.3	7	95	0.03
Fugitives II[1]	100	37	53	4400	0.27
Thermox on purge	875	642	784	400	3.92
Other					
SCR	1 870	114	418		2.09
WAO	5 000	360	1170		5.86
Ground protection	50	3	3		0.01

[1] *Incremental costs of second stage shown*

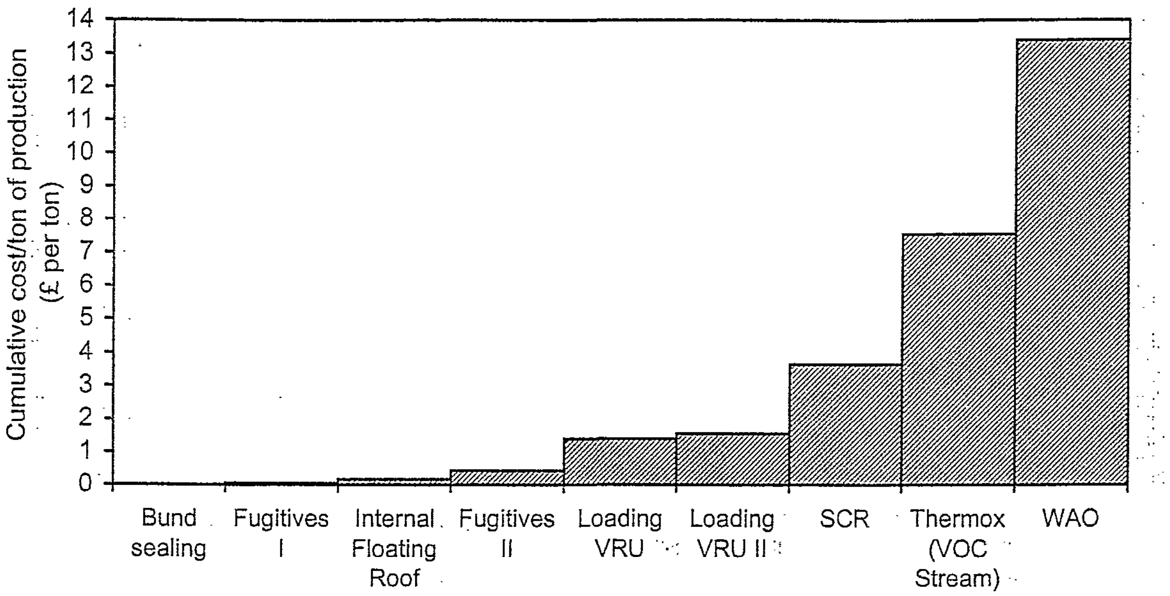


Figure 6.9 **Cumulative cost of abatement measures: generic petrochemical plant**

6.2.4 Economic impact of abatement techniques

The costs of abatement will, in a commodity chemical business, reduce the business profitability rather than being passed on to customers. A true analysis of impact on competitive position would need a review of the control requirements in competitor countries, which is beyond the scope of this report. It terms of defining BATNEEC rather than BAT, it could be suggested that, in addition to the best practice within an industry, average practice is also a useful marker.

The economic information presented in Section 6.2.2 permits the costs of abatement to be placed in some context. It could tentatively be suggested that an additional cost of one pound sterling per ton of product, while not insignificant, would not be economically crippling. Within the context of the differences between Leader and Laggard plants, and the historic margins, an additional cost of £10 per ton would be very important in several cases and might have negative implications for the business. This suggests, for the hypothetical case considered, that bund sealing, measures to control fugitive emissions, and floating roofs are economically reasonable measures. It should be noted that the cost per ton abated of some measures, such as the second stage of VRU on loading, is high, so this is not necessarily good value for money. This is not shown on the graph because it includes control of different pollutants.

It is implicit in this analysis that new abatement costs are not added each year. If the four-year period between revisions of authorisations is taken as the basis, the capital charges would need to be very much higher than those in the report, which are based on a ten year period. The implication of this is that industry economics would need to be reviewed periodically, or the calculations of costs of abatement should assume a very rapid write-down.

6.3 Formaldehyde

6.3.1 Industry characteristics

Formaldehyde is one of the most widely used chemicals. The largest use is in resins such as urea-formaldehyde, phenol-formaldehyde, and melamine formaldehyde. Wood chip products are a major end-use, and producers are often integrated downstream into resin production or even into manufacture of wood products. Other uses of formaldehyde include the production of polyhydric alcohols and of butanediol, although the latter is challenged by new process routes that are based on other feedstocks. Formaldehyde is also one of the feedstocks in the production of MDI, an isocyanate used to produce polyurethanes (see Section 6.7).

There are six manufacturers of formaldehyde in the UK, with capacities ranging from a few thousand tons per year to over 100 000 tons per year.

The feedstock for formaldehyde production is methanol, which is itself produced almost exclusively from natural gas. Methanol prices are driven by demand factors, such as MTBE consumption in gasoline, and international supply capability. In 1995, a global imbalance caused European prices of methanol to surge to US $300 per ton compared to a more usual US $100-150 per ton. Methanol prices do not necessarily follow the petrochemical business cycle described in Section 6.2, so there is some degree of decoupling from the petrochemical industry.

6.3.2 Industry economics

The cost of formaldehyde production is dominated by the price of methanol, which is usually purchased from third parties. Table 6.7 shows an approximate cash cost of production for formaldehyde in 1997, not specific to either main type of process. The variable cost includes a small credit for steam, but is mostly the cost of methanol. Large scale purchasers of formaldehyde often agree a price formula that includes the price of methanol. For producers integrated downstream, as many are, this may not eliminate risk as there will be an upward pressure on the price of the finished product, and a downward pressure on margins, if methanol prices fly up.

Table 6.7 Cash costs of production of formaldehyde, typical Western Europe, 1997

Element	Unit	Data
Capacity	ton per year (37%)	50 000
Capital cost	£ million	11
Variable cost	£ per ton (37%)	38
Fixed cost	£ per ton (37%)	20
Cash cost	**£ per ton (37%)**	**58**

A typical cash cost margin on formaldehyde is around £20 to £35 per ton of 37 percent solution. Much of the consumption is in integrated downstream units or on long term contracts, so transfer prices depend upon negotiation in each circumstance.

6.3.3 Costs of abatement

The techniques identified to illustrate costs of abatement are summarised below. The costs are presented in Table 6.8.

- Methanol, which is typically stored in atmospheric tanks, has a moderately high vapour pressure. Even with a nitrogen pad system, there will be losses on tank loading. For formaldehyde, the environmental impact of the material - rated as 'medium' - supports a case for control. Balance lines and a simple vent scrubber system are roughly costed, with the scrubber effluent joining the main process scrubber steam. This is illustrative only as Chem Systems has not identified examples where this is installed.

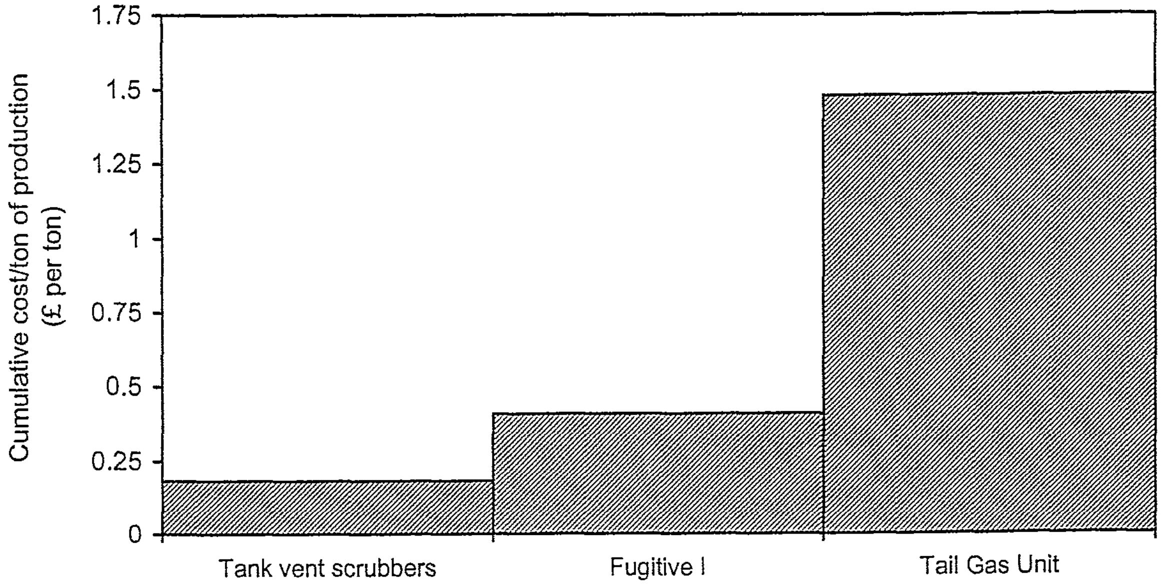
- Fugitive emissions are generally low. There is the possibility of installing high integrity equipment and fittings, as noted in Section 5.2. This is not included in the economic review because it is most appropriate for new plant. As an add-on technique, a simple leak detection and repair programme is considered.

- Tail gas incineration, as described in Section 5.2, is the final option. The technology considered is that applying to the metal oxide process. The VOCs removed include dimethyl ether, methanol, and formaldehyde itself. Carbon monoxide is also oxidised. A conservative economic case is calculated, with no credit given for steam production. If there is a beneficial use for the steam, the net cost of incineration is decreased. Both cases are shown in Table 6.8, but only the conservative case appears on Figure 6.10.

Table 6.8 Costs of abatement: formaldehyde production

Technique	Capital cost *£000*	Operating cost *£000 pa*	Annualised cost *£000 pa*	Cost/ton of VOC *£*	Cost/ton of product *£*
Tank vent scrubbers	45	2	9	3040	0.18
Fugitive I	8	10	11	2730	0.22
Tail gas unit	250	13	54	146	1.07
Tail gas unit (steam credit)	250	-17	24	65	0.47

In the context of the cash costs of production of formaldehyde, and the range of cash cost margin, these costs are certainly significant but probably not crippling. The hypothetical cases of tank vent scrubbers and fugitives detection appear relatively inexpensive in terms of annual cost, but are expensive in terms of approximate cost per ton VOC abated. As with petrochemicals, the calculation is made on the basis of a one-off investment.



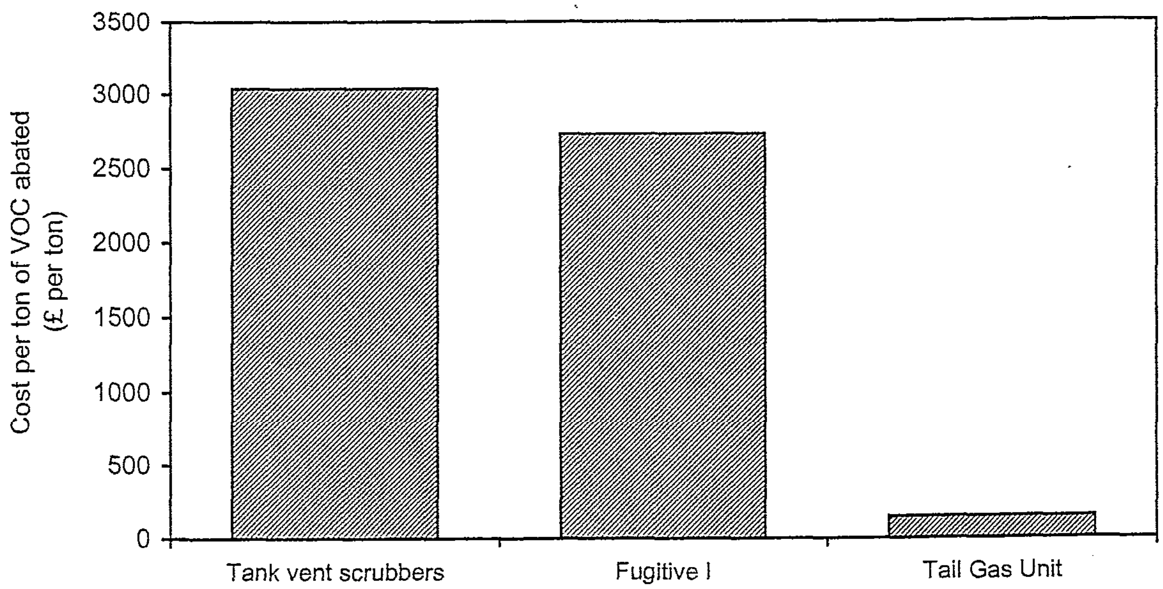


Figure 6.10 Cost of abatement measures: formaldehyde plant (cumulative annual cost and cost per ton VOC)

6.4 Polyolefins

6.4.1 Industry characteristics

Production of polyolefins is one of the areas reviewed in Section 5. The polyolefins included in this category are commodity polyethylenes, (Low Density Polyethylene, Linear Low Density Polyethylene and High Density Polyethylene and variants, and Polypropylene). These are known by the acronyms LDPE, LLDPE, HDPE and PP.

Table 6.9 lists polyolefin plants in the UK. The feedstocks to the polyolefin plants are ethylene and propylene, for polyethylenes and polypropylene respectively. Ethylene and propylene are both obtained from steam crackers; propylene is also a refinery by-product. All the producers are majors in the commodity petrochemical business and there is often integration with feedstock supply, either within one company or in established commercial arrangements.

Table 6.9 Polyolefin Manufacture in the UK

Process	Company	Capacity *(thousand tons per year)*	Year of Start-Up	Last Extension	Ownership Pattern/ Other Information
LDPE	Montell, Carrington	65	Pre-1976	1993	Formerly Shell. Merged with Himont in 1994. Montell from 31/03/95
	Montell, Carrington	120	1993	1996	Formerly Shell. Merged with Himont in 1994. Montell from 31/03/95
LLDPE	BP, Grangemouth	250	1990	1997	-
HDPE	BP, Grangemouth	280	Pre-1976	1997	-
PP	Appryl, Grangemouth	250	1999	-	-
	Targor, Wilton	100	1981	-	Formerly ICI. Sold to BASF Jan 94. Targor Jun 97
	Targor, Wilton	60	1988	1996	Formerly ICI. Sold to BASF Jan 94. Targor Jun 97
	Montell, Carrington	165	1990	1996	Formerly Shell. Merged with Himont in 1994. Montell from 31/03/95

The economic dynamics of the commodity polymer business are broadly similar to those for commodity petrochemicals. The nature of the market, however, differs in a number of aspects:

- consumers are plastics processors of varying sizes rather than (usually large) chemical companies; distribution networks and customer service are particularly important
- plastic products compete directly with each other and with other materials in many applications
- polymers must satisfy many requirements both for processability and to provide the required attributes of the packaging or other end product.

Intensive development has been undertaken in the past decade to improve production technology and to provide polymers with desirable characteristics. There has been a shift from LDPE to LLDPE/HDPE plants, and an increase in scale.

Commodity polymers is an increasingly global business, with a move towards large players that focus on certain core business areas. As well as reduced corporate costs, the larger players aim to provide good market coverage and customer support. A number of the major producers in Europe are now joint ventures between companies consolidating a position in specific products. Examples include Montell, Targor, and Borealis.

Western Europe as a whole has been suffering increasing competition from other regions, especially the Middle East with its low cost hydrocarbon feedstocks. The UK is a large net importer, as Table 6.10 indicates, although this masks the fact that there are both exports and imports.

Table 6.10 Net UK Export/(Import) of polyolefins

		1993	1994	1995	1996[1]
LDPE	*(000 ton)*	(310)	(330)	(325)	(350)
	(% consumption)	(58)	(62)	(62)	(64)
LLDPE	*(000 ton)*	(157)	(165)	(172)	(210)
	(% consumption)	(63)	(60)	(60)	(65)
HDPE	*(000 ton)*	(240)	(230)	(240)	(235)
	(% consumption)	(57)	(53)	(53)	(50)
PP	*(000 ton)*	(280)	(375)	(353)	(385)
	(% consumption)	(49)	(58)	(56)	(57)

6.4.2 Industry Economics

Polyolefins are covered by Chem Systems' PPE programme and this section employs data from that source. As with petrochemicals (Section 6.2), Chem Systems uses the concept of Leader and Laggard plants to represent more competitive and less competitive plants respectively. Another similarity with basic petrochemicals is the cyclicality of the business; polyolefins are part of the same cycle.

a) *Costs of production*

Table 6.11 shows the cost of production of polyolefins for West European leader plants. In each case, the feedstock olefin (ethylene or propylene) is priced at market value, or published West European contract price. For an integrated cracker plus polyolefin plant, the olefin might be transferred by the company at cash cost of production. However, the merchant price basis is the better representation of the polyolefin plant as a stand-alone unit.

Feedstock costs dominate the variable costs and the total costs of production. The costs of production therefore fluctuate strongly with the business cycle.

Table 6.11 Cash costs of production for selected commodity polyolefins, Leader plants, Western Europe, 1997 Prices

		LDPE	LLDPE	HDPE (impact)	HDPE (blow mould)	PP
Capacity	kt/a	200	220	220	130	230
Total Capital	£ million	53	53	53	38	63
Total Variable Costs	£/t	397	399	392	390	327
Total Fixed Costs	£/t	21	19	20	27	19
Tech Service & Sales	£/t	21	21	21	21	21
CASH COST	**£/t**	**439**	**439**	**433**	**438**	**367**
Freight	£/t	39	39	39	39	39

b) *Profitability*

Cash cost curves of LDPE, LLDPE and HDPE are shown as figures 6.11-6.13. The curves are relatively flat because the purchased ethylene is a large part of the cost.

The differences between the costs of production of West European Leader and Laggard plants are shown in Table 6.12. This is a broad indicator of the potential for margins for more economic producers.

Table 6.12 Difference Between Leader and Laggard Cash Costs for Polyolefins, Western Europe, 1997 Prices

Polymer	Leader £/t	Laggard £/t	Difference £/t
LDPE	439	492	53
LLDPE	439	491	52
HDPE (impact)	433	489	56
HDPE (blow mould)	438	489	51
PP	367	442	75

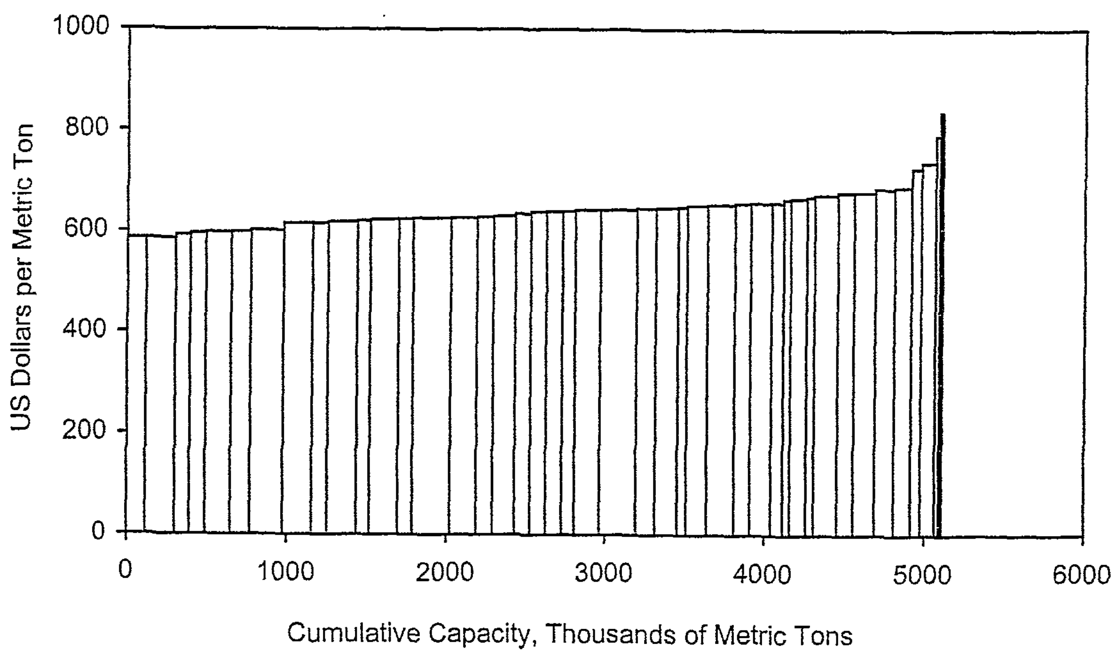


Figure 6.11 Cash cost curve for LDPE, Western Europe

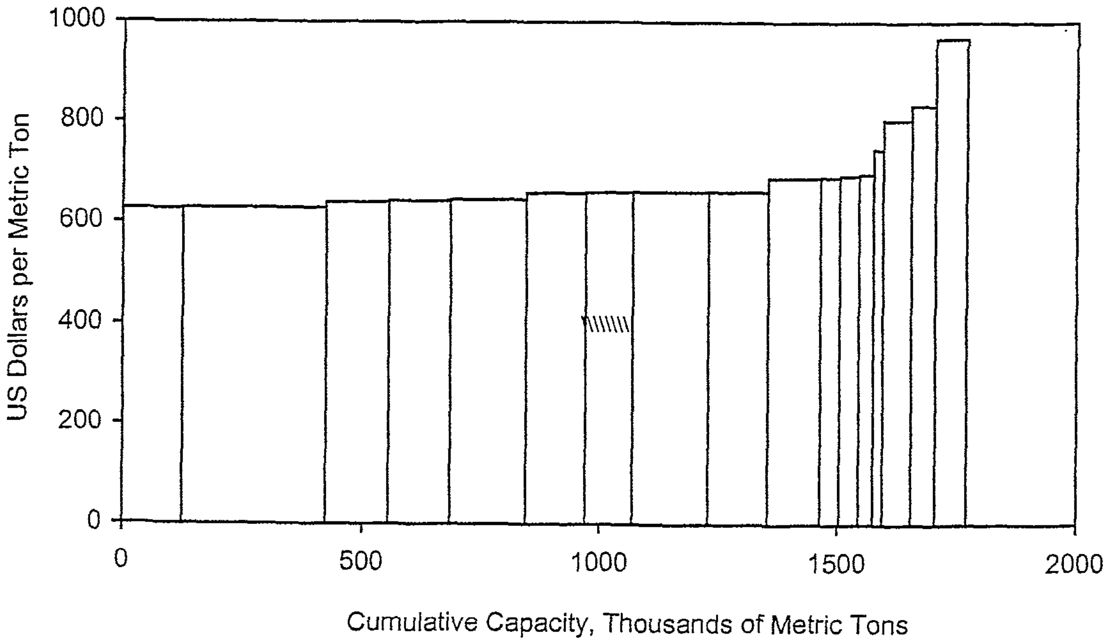


Figure 6.12 Cash cost curve for LLDPE, Western Europe

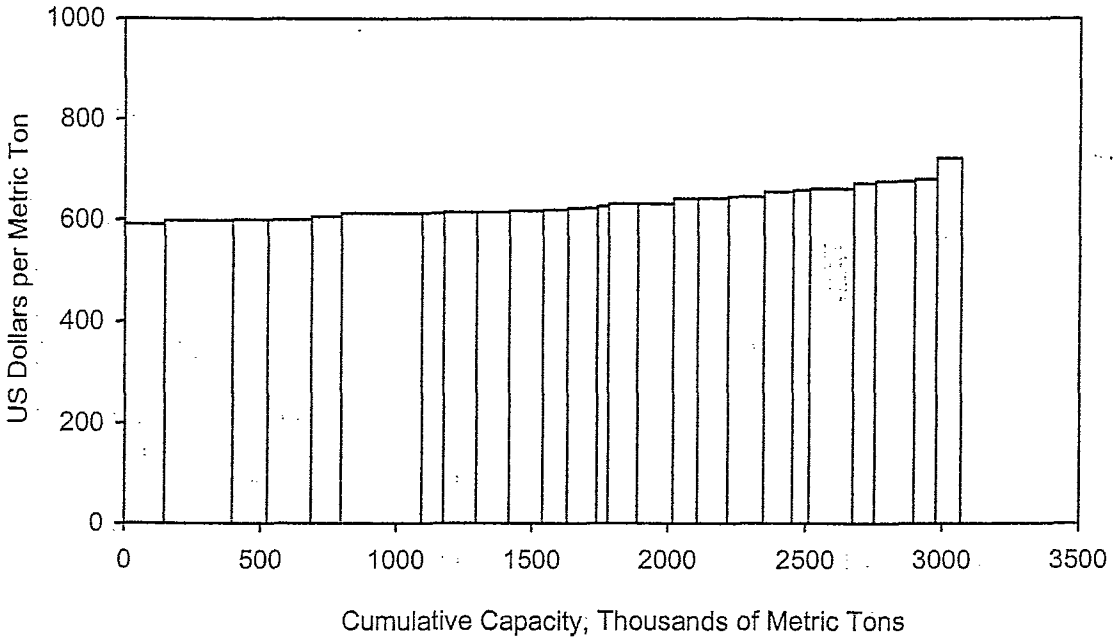


Figure 6.13 Cash cost curve for HDPE, Western Europe

Figures 6.14-6.18 shows the cash cost margins for West European Leader and Laggard plants. The margins (on a purchased olefin basis) follow the business cycle and, even for leader plants, may be negative in the business trough. The conclusions are the same as for basic petrochemicals:

- changes in cost cannot be passed on to consumers
- cash flow will be low or even negative at some part of the business cycle
- margins and costs fluctuate so that care is needed in quoting environment costs as a percentage of either
- the position of a company in the cash cost curve influences its own views of its long-term prospects and thus its willingness to invest or to leave the business.

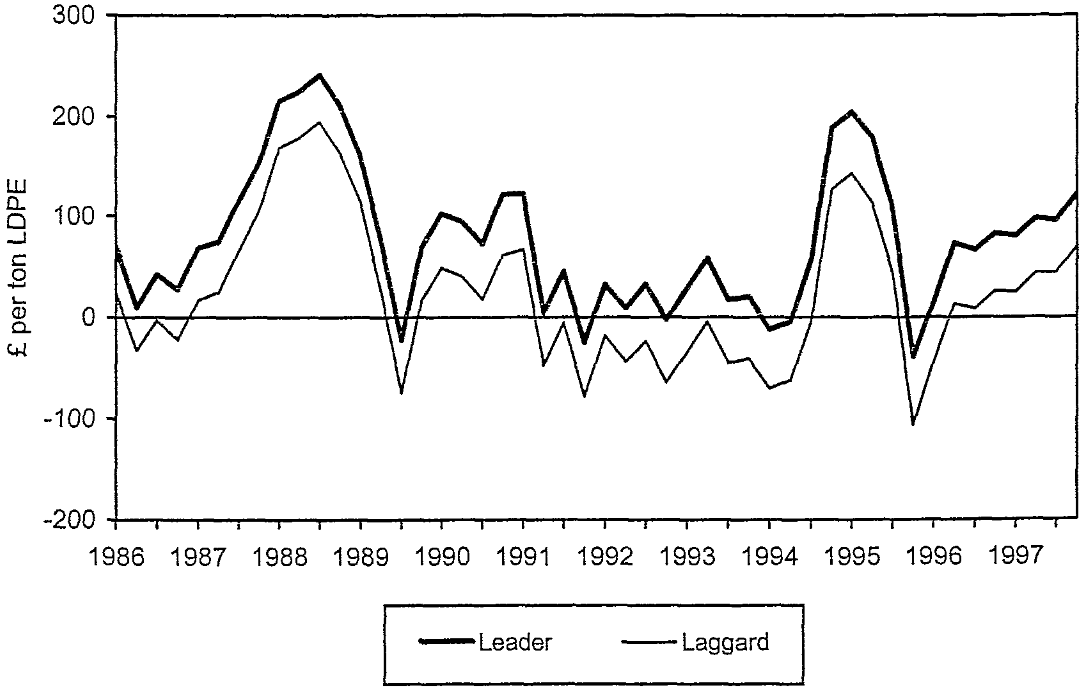


Figure 6.14 Cash cost margin for LDPE, Western Europe

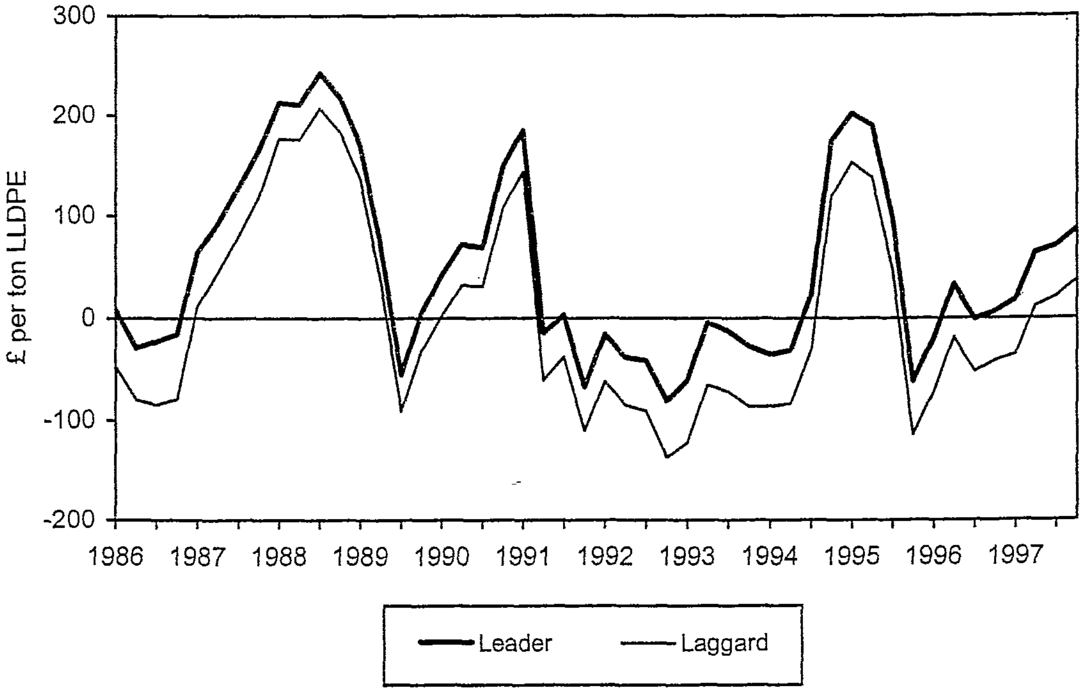


Figure 6.15 Cash cost margin for LLDPE, Western Europe

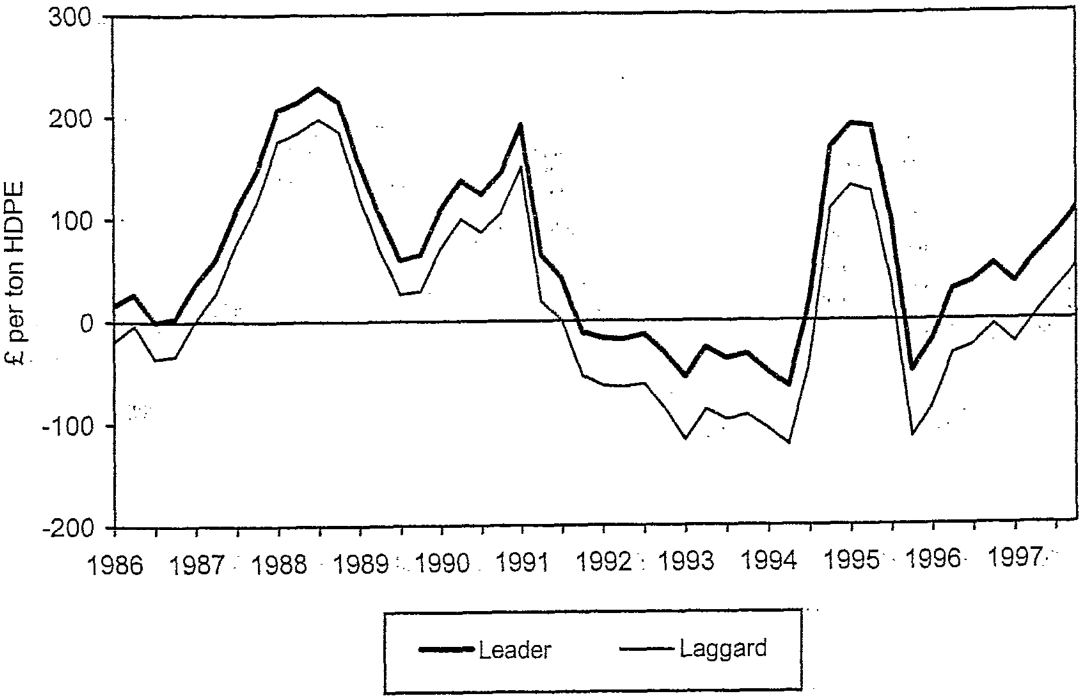


Figure 6.16 Cash cost margin for HDPE (impact), Western Europe

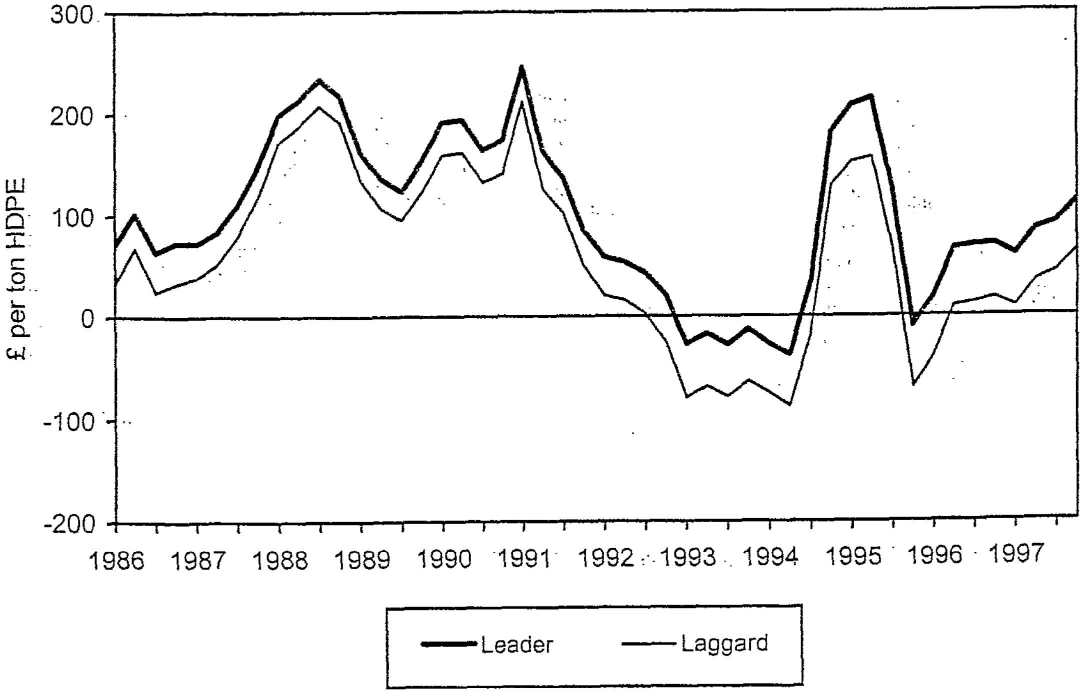


Figure 6.17 Cash cost margin for HDPE (blow mould), Western Europe

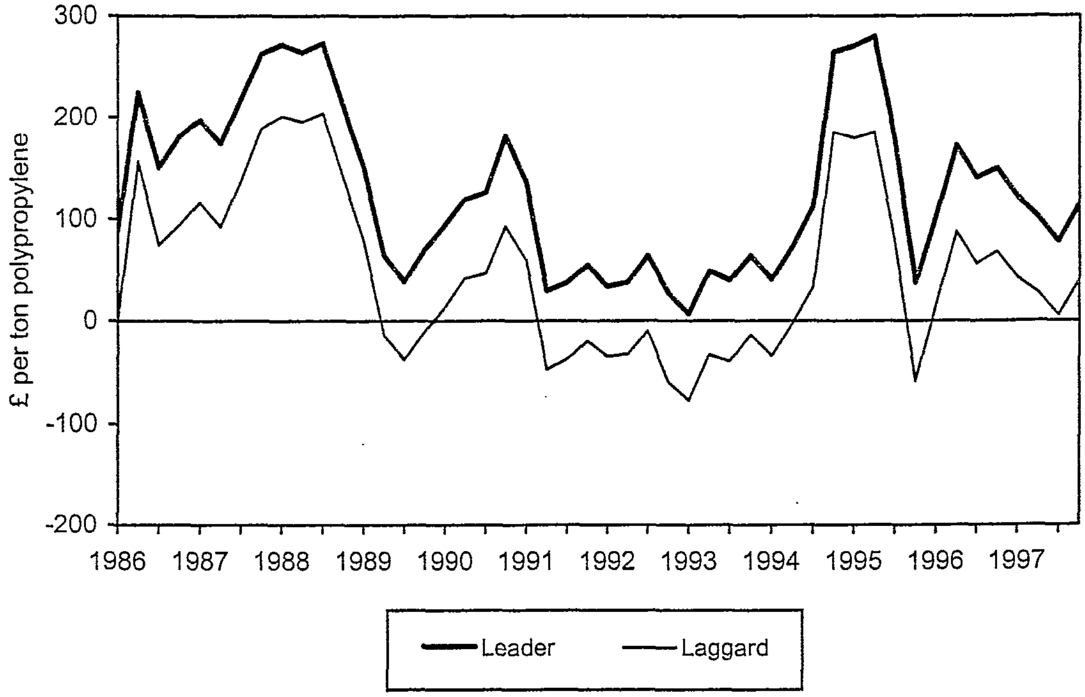


Figure 6.18 Cash cost margin for Polypropylene, Western Europe

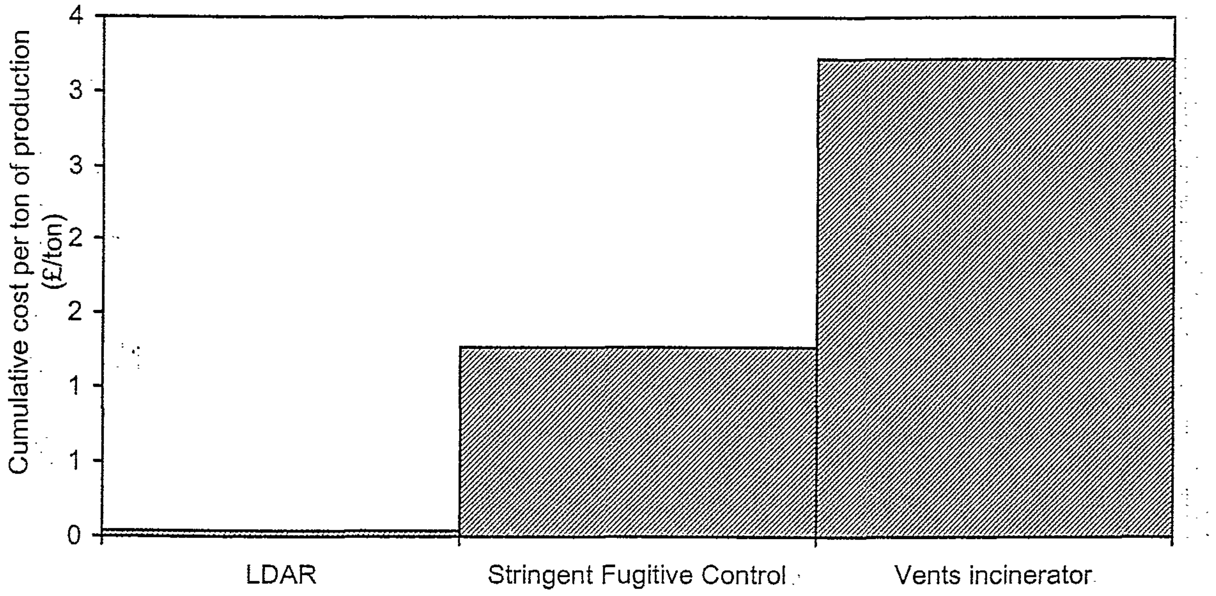
6.4.3 Costs of abatement

The techniques described for LDPE plants (Section 5.3) are used here as examples in the context of industry economics. Table 6.13 shows the cost estimates.

Table 6.13 Costs of abatement: LDPE production

Technique	Capital cost *£000*	Operating cost *£000 pa*	Annualised cost *£000 pa*	Cost/ton of product *£*	Cost/ton of VOC *£*
Vent collection and incineration	465	108	183	1.83	375
LDAR	40	(3)	4	0.04	33
More stringent fugitives control	450	50	123	1.23	6 160

In the context of industry economics, the simple LDAR scheme is clearly not a major burden, but it is difficult to draw firm conclusions on affordability. The more stringent control of fugitives is relatively costly per ton of VOC abated. Figure 6.19 shows the results graphically.



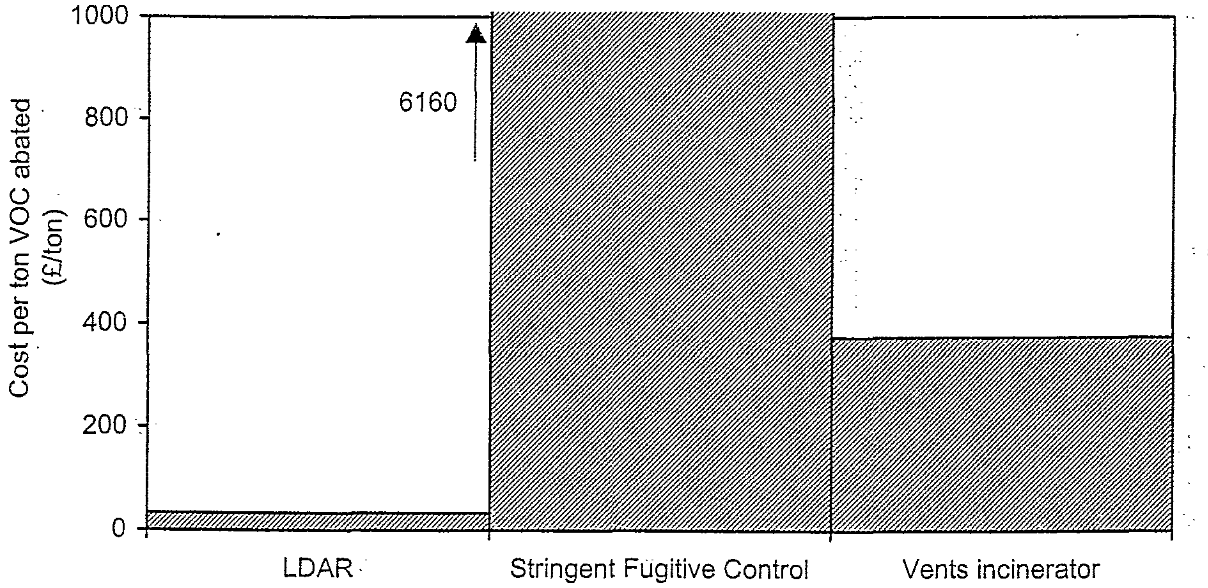


Figure 6.19 Cost of abatement measures: LDPE plant (cumulative cost per ton product and cost per ton VOC)

6.5 EDC/VCM/PVC

6.5.1 Industry characteristics

The EDC/VCM/PVC chain is one of the cases reviewed in Section 5. The main feedstocks to the chain are chlorine and ethylene. In practice, there is a high degree of integration with feedstock production, particularly chlorine production. The merchant market for chlorine is small, partly because of the implications of transporting chlorine. The EDC/VCM/PVC chain is by far the largest single chlorine consumer, so integration with chloralkali plants is common.

Table 6.14 lists the production plants in the UK. The companies are named to indicate the degree of integration. It should be noted that EVC was initially a joint venture between ICI and Enichem of Italy. The link of chloralkali and EDC/VCM/PVC still exists, although EVC is now a separate company. Some plants are relatively old but have, mostly, been extended recently.

Table 6.14 EDC/VCM/PVC Manufacture in the UK, 1997

Process	Company	Capacity (000 ton per year)	Year of Start-Up	Last Extension	Ownership Pattern/ Other Information
EDC	EVC, Hillhouse	190	Pre-1976	1994	-
	ICI, Runcorn	260	Pre-1976	1996	Formerly EVC. Bought by ICI in 1995
	EVC, Runcorn	215	Pre-1976	-	Part of VCM facility
	ICI, Wilton	250	1984	-	Non-integrated
VCM	EVC, Hillhouse	190	Pre-1976	-	
	EVC, Runcorn	180	Pre-1976	Planned 1998 (+120)	Formerly EVC. Sold to ICI in 1995. Bought back by EVC in 1996
PVC	EVC, Barry	125	Pre-1976	1991	-
	EVC, Hillhouse	40	Pre-1976	1991	Emulsion PVC
	EVC, Runcorn	105	Pre-1976	1996	-
	Hydro Polymers, Aycliffe	190	Pre-1976	1997	Formerly BIP. Cpd facility j.v. with BF Goodrich from 1991

Economic drivers are larger similar to other commodity petrochemicals, with some differences.

- There are two products to chloralkali plants: chlorine and caustic. When the demand for PVC is high, caustic must be co-produced with the chlorine and so tends to over-supply. The net cost of chlorine, after allowing a credit for caustic sales, may vary counter to the petrochemical business cycle for this reason.

- EDC and VCM are traded inter-regionally to some extent. Almost all is used for PVC production, however, so the economics are closely linked to those of PVC in the consuming region.

- As with polyolefins, PVC competes with other plastics and other materials, and is sold to processors with particular processability or product needs. PVC may be sold compounded with other materials for specific applications.

One area of interest is the future of the PVC business. PVC has suffered pressure from environmentalist groups such as Greenpeace. The concerns relate to the production processes in the total chain, the effects of certain additives used in PVC products, and the possible impacts on disposal. The validity or otherwise of the environmentalists' arguments is not as relevant in this context as the empirical consequences of the pressure. Chem Systems' own forecasts show a slow but steady growth in PVC demand. The decline in consumption in some packaging applications, particularly in certain West European countries, is compensated by the strong position of PVC in construction applications. Construction applications account for around 67% of the West European market. In general, however, PVC is a relatively mature product.

The producer industry has responded to concerns related specifically to pollution from production processes. Section 5 describes the abatement techniques now available and in use.

The UK imports around one half of the PVC it consumes; total consumption is over 700 000 tons per year. Production of EDC and VCM is largely dedicated to PVC production. There is a small import of VCM and a small export of EDC.

6.5.2 Industry Economics

Data on EDC/VCM/PVC are drawn from Chem Systems' PPE programme. The economics of chloralkali production are included in these analyses for the reasons given above, although chloralkali plants do not fall into the category of petrochemicals and large scale organic processes.

a) Costs of production

Table 6.15 shows the cost of production of chlorine (presented as the cost of production of one Electrochemical Unit, or ECU, which is one ton of chlorine plus 1.1 tons of caustic), EDC, VCM and PVC West European Leader plants. The EDC plant is one producing EDC as an export product rather than part of an integrated EDC/VCM facility. The PVC leader is a suspension process. Feedstock ethylene is costed at purchase price. Chlorinated feedstock to any step – chlorine, EDC or VCM – is included at production cost, assuming upstream integration. The bases on which the feedstocks are costed differ between products to match the usual business situation. The cost of chlorine as a feedstock includes a credit for caustic co-product sales, for example.

Table 6.15 Cash costs of production for EDC/VCM/PVC Leader plants, Western Europe, 1997 Prices

		Chlorine	EDC	VCM	PVC
Capacity	ktpa	252	289	410	220
Total Capital	£ million	161	26	133	103
Total Variable Costs	£/ton	112	114	203	251
Total Fixed Costs	£/ton	48	43	56	74
Tech Service & Sales	£/ton	-	-	-	21
CASH COST	**£/ton**	**160**	**157**	**259**	**346**
Freight	£/ton	-	10	10	36

The feedstock costs are very important parts of the total cash cost. For chlorine, the cost of electric power is also very significant. The total costs of EDC/VCM/PVC will vary with that of both ethylene and chlorine, suggesting partial decoupling from the petrochemical business cycle.

b) Profitability

As with other products, the differences between Leader and Laggard costs of production are an indicator of the potential margin for more economic producers. Table 6.16 shows the data.

Table 6.16 Difference between Leader and Laggard Cash Costs for EDC/VCM/PVC, Western Europe, 1997 Prices

Product	Leader £/t	Laggard £/t	Difference £/t
Chlorine	160	228	68
EDC	157	219	62
VCM	264	311	47
PVC	346	431	85

Figures 6.20-6.23 show historical data. Figures 6.20 shows the net cash cost of chlorine after caustic credit. The graphs for EDC, VCM and PVC show cash cost margins. For VCM and PVC, product is priced on a delivered domestic contract basis. EDC margins are those for export, which might involve a comparatively low netback on prices in Asia, for example.

Although the shapes of the curves are a little different to those of basic petrochemicals and polyolefins, the message is similar. These are commodity products in which cost increases can not necessarily be passed on to consumers. The variability of margins makes it difficult to draw numerical conclusions. There is a range of economics between plants, and the business situation for those at the poor end is not attractive in times of down turn.

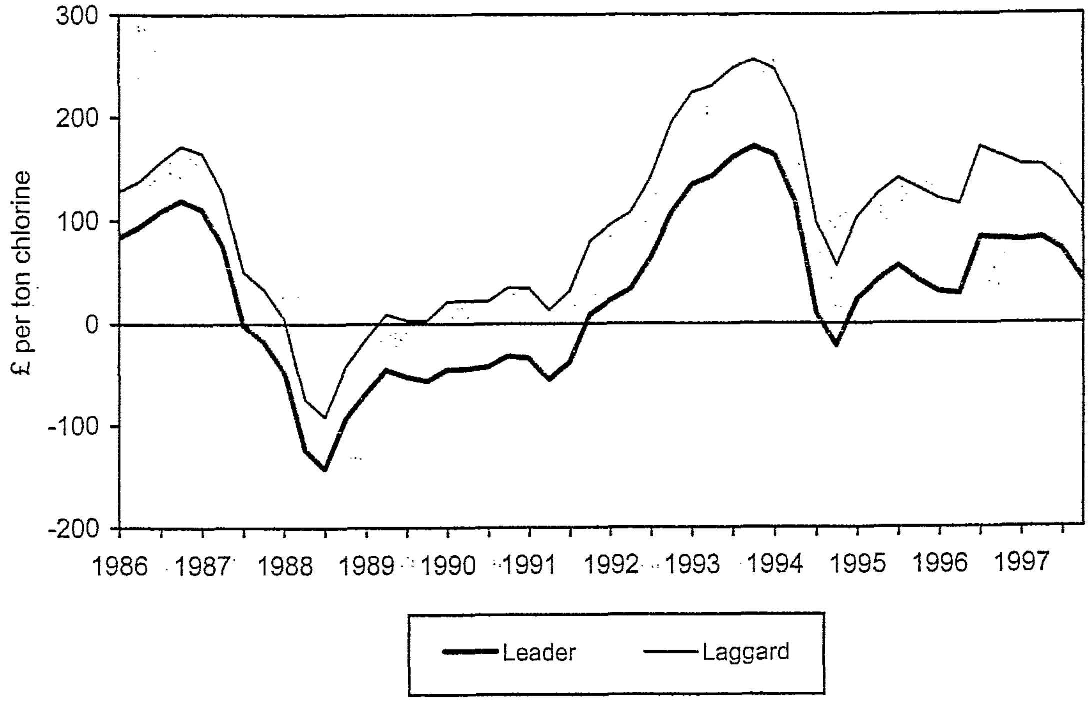


Figure 6.20 Cash cost (net of caustic) for chlorine, Western Europe

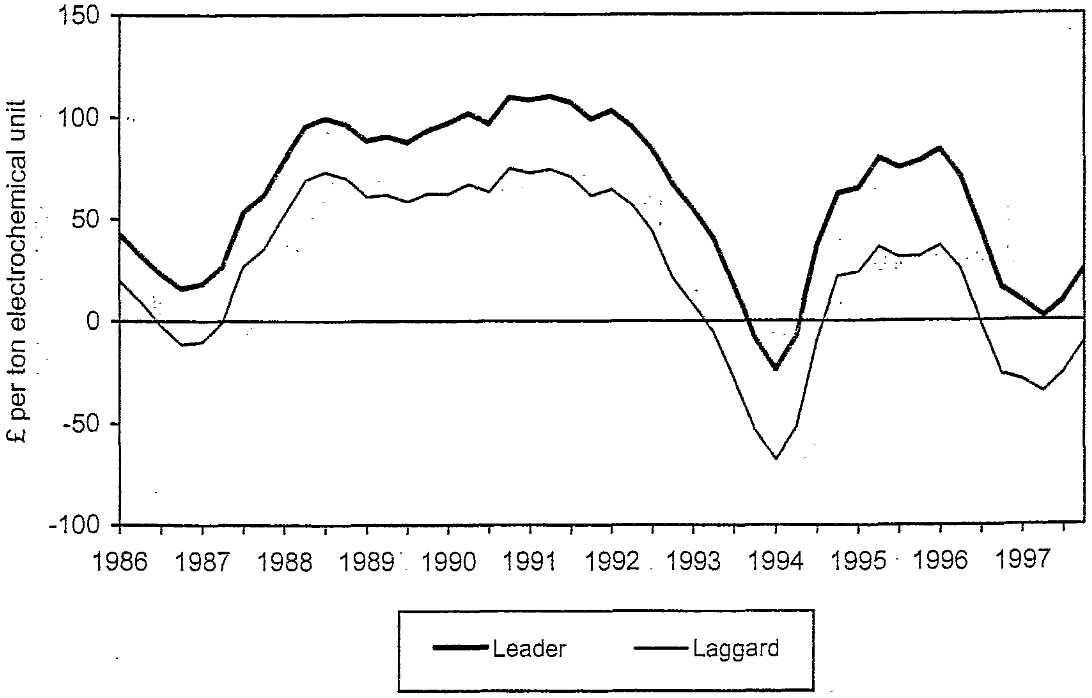


Figure 6.21 Cash cost margin for EDC, Western Europe

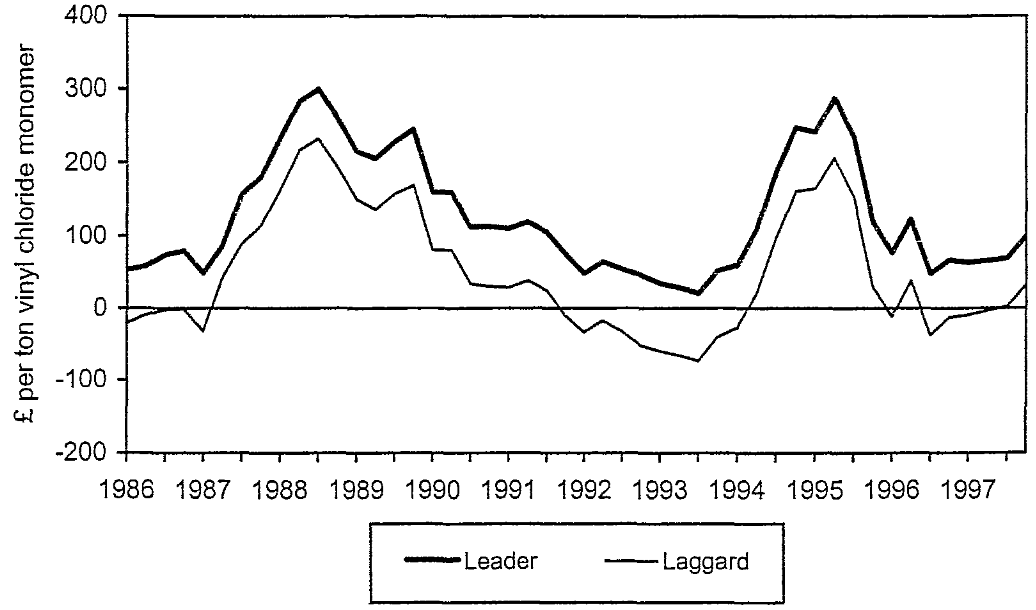


Figure 6.22 Cash cost margin for VCM, Western Europe

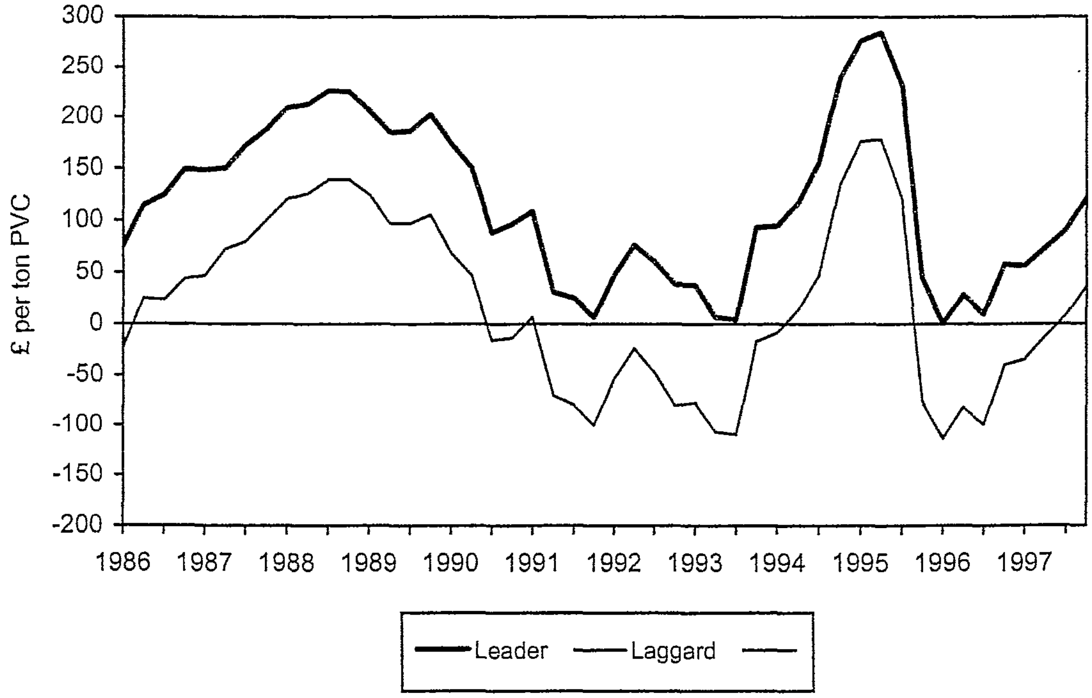


Figure 6.23 Cash cost margin for PVC, Western Europe

6.5.3 Costs of abatement

Pollution abatement techniques for EDC, VCM and PVC plants are described in Section 5.4. Several of the techniques are already applied on UK plants. The purpose of this part of the report is to put the costs of abatement into the broad context of industry economics. To do this, a number of possible techniques are selected for EDC/VCM and, separately, PVC.

EDC/VCM

A combined and balanced EDC/VCM plant with a capacity of 200 000 ton per year VCM is taken as the basis. Oxygen-based oxychlorination is assumed. It is recognised that EDC and VCM plants are not necessarily integrated, but the cost of production estimates in Section 6.5.2 assume an integrated facility. The techniques examined are as follows.

- Installation of high integrity equipment throughout, such as sealless pumps and valves with bellows to control fugitive emissions. This is assumed to occur progressively, when substantial maintenance or renewal is undertaken, rather than as a forced retrofit. The cost estimate is a very approximate indicator of cost differential with conventional equipment.

- Ducting of miscellaneous vents, such as from relief systems, to a vent gas incinerator. An incinerator is only one of the possibilities here. It is assumed that supplementary fuel is needed.

- High temperature incineration of liquid and tarry chlorinated organic wastes, with recovery and sale of hydrochloric acid. The waste incinerator and the vents incinerator are considered as two items, although combining them may be feasible.

- Steam stripping of EDC from wastewater and return to process.

- Water treatment facilities including precipitation of copper compounds, conversion of difficult organics and stripping of chlorinated decomposition products.

Table 6.17 and Figure 6.24 show broad estimates of costs of these techniques. In the context of the costs of production and profitability information presented in Section 6.5.2, several of the abatement costs are very significant. However, potential pollution from this type of facility includes VCM and dioxins and so is of high environmental significance. In addition, producers in Western Europe have a policy to move towards good practice, so that West European competitors at least face a similar economic burden.

Table 6.17 Costs of abatement: EDC/VCM production

Technique	Capital cost *£000*	Operating cost *£000 pa*	Annualised cost *£000 pa*	Cost/ton VCM *£*
Vents incinerator	2 000		325	1.51
Organics incinerator	6 000	-254	721	3.28
Fugitives (equipt)	500	5	86	0.39
EDC stripping	500	209	290	1.32
Other WWTP	1 800	77	370	1.68

PVC

For PVC, a suspension process with a capacity of 220 000 tons per year is taken as basis. It is assumed that the plant is already fitted with adequate strippers to remove VCM from the reaction slurry. This is key to control of VCM emissions and such stripping equipment should be mandatory. It is also assumed that VCM monitoring in the workplace is carried out continuously; this is largely an occupational health issue rather than an environmental question.

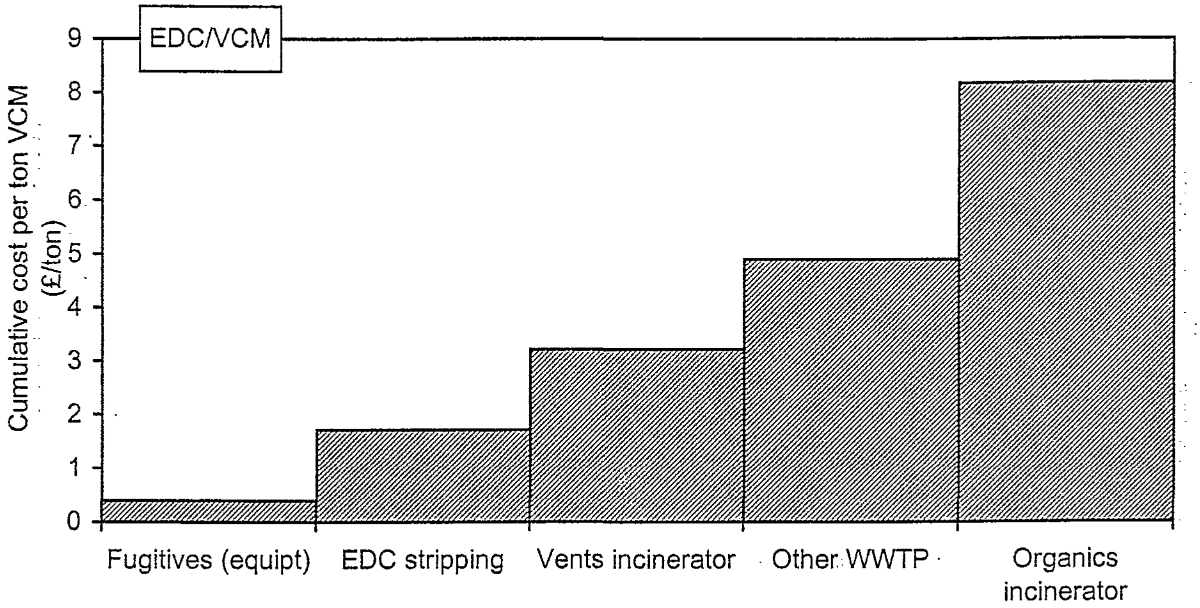
Additional measures are selected for illustration as follows:

- As with VCM production, the progressive installation of high integrity equipment and fittings is taken as one technique.
- Improvements to the reactor system to minimise the frequency of opening. Use of anti-scaling chemicals and installation of internal sprays are examples. A nominal capital sum is included in the cost estimate but no allowance is made for any possible labour saving.
- Removal of VCM from the recovery system condenser vent. The economics are based on a membrane system, but other techniques such as carbon adsorption and absorption in liquid organics are also feasible and used.
- Wastewater stripping to 1 mg/litre VCM.

Indicative costs of abatement are presented in Table 6.18 and on Figure 6.24. As with the costs on the EDC/VCM facility, the costs are significant in the context of industry profitability but are, or will be, also borne by competitors in other West European countries.

Table 6.18 Costs of abatement: PVC

	Capital cost *£000*	Operating cost *£000 pa*	Annualised cost *£000 pa*	Cost/ton PVC *£*
Improved reactor system	1 000	0	163	0.74
VCM recovery	490	-64	16	0.07
Fugitives (equipt)	350	9	66	0.30
Water treatment/recycle	500	300	380	1.73



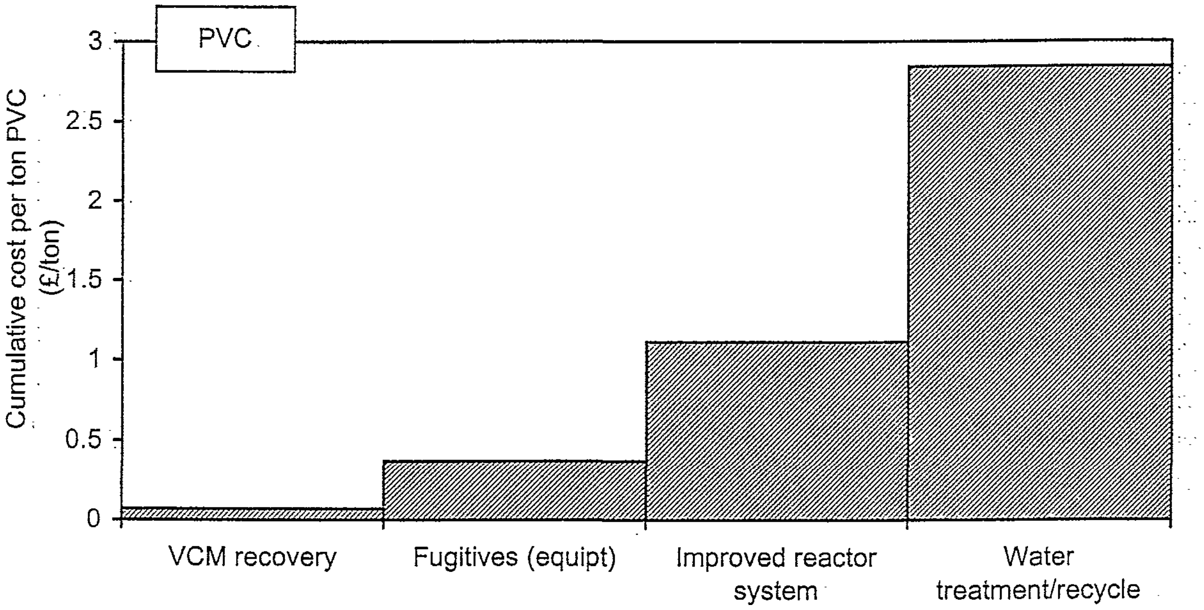


Figure 6.24 Cumulative cost of abatement: EDC/VCM and PVC plants

6.6 Emulsion polymers

6.6.1 Industry characteristics

Emulsion polymers are principal components in the manufacture of a wide variety of products, including paints and coatings, adhesives, paper, carpet backing, textiles and others. Four major groups are made in the UK and Western Europe:

- acrylics (all acrylic, styrene acrylic, vinyl acrylic)
- polyvinyl acetate
- styrene butadiene
- vinyl acetate–ethylene (VAE).

There are many emulsion polymer plants in the UK, including Vinamul (now ICI), Harlow Chemicals. Doverstrand, Bayer, Viking Polymers and Enichem in Hythe, amongst others. The principal characteristic of the business is a result of a 50 percent solution, which is the end product (except for VAE powders). This leads to many plants being built in each country due to excessive logisitic costs for moving dilute solutions to a very high number of local clients. The business requires a high degree of technical service to meet the demands of such a wide diversity of client needs. Plants are multi-purpose for acrylics and vinyls such as Vinamul Warrington and single purpose for VAE and SB/SBR latex at Enichem Hythe, Southampton. Total volumes of emulsion polymers in Europe are over 1 million tons per year with styrene butadiene latex the largest volume.

Many plants are in the 10 to 20 year vintage and are thus in the retrofit category for installing new abatement techniques.

VAE is the product with the highest growth potential among this group, mainly to the adhesives, coatings and powder markets, and is the subject for the economic case study. Vinamul at Warrington, for example, produces VAE along with other emulsion polymers. Recent years have seen an increasing demand for VAE both as a 50 percent solution and spray dried powder form in the constructions industries. Spray drying is used in Germany, Holland, principally for the competitors of Vinamul such as Hoechst, Wacker; Vinamul has its own plant in Geleen, Holland.

6.6.2 Industry Economics

VAE is less of a commodity product than other emulsion polymers. Nevertheless it follows conventional commodity economics, i.e. a cash cost of production plus a margin determined by supply/demand balances. Indicative cash costs of production in Western Europe are shown in Table 6.19.

Table 6.19 Cash costs of production for VAE, Western Europe, 1997

	Low cash cost (£/ton)	High cash cost *(£/ton)*
VAE	700	920

The costs are calculated on the site specific circumstances and unit costs. Some producers are back integrated into Vinyl Acetate Monomer and Ethylene. The margin varies between £200 and £400 per ton based on current sales prices.

6.6.3 Costs of abatement

VAE is included as a process case because it is typical of speciality chemicals in the sector and has to deal with VOC abatement. There are several other pollution control requirements, but the purpose of the section is to highlight major cost items in the context of production economics.

Various high temperature incinerators have been employed in Europe. Economics are based on a 20 000 ton per year VAE plant (at 50% solids).

The cost assumes a market price for fuel which is site/county specific.

Table 6.20 Cost of treatment of VOC abatement VAE plant

Technique	**Cost per ton VAE** *(£/ton)*
Incineration	15

Within the context of the economics of the business, the costs of pollution control are significant. However, several West European plants are being required to install similar abatement within this business sector dependent on the locality of the plant.

6.7 Nitrobenzene/aniline

6.7.1 Industry characteristics

Production of nitrobenzene and aniline is selected as an economic case study because the pollution control requirements are significant and because this industry sub-sector has its own characteristics.

Almost all nitrobenzene is used to make aniline. The main use for aniline is in the production of MDI (methylene diphenyl di-isocyanate), which accounts for over 80 percent of West European aniline consumption. The end-use in this chain is the production of polyurethane goods. Polyurethane is made in-situ by the reaction of polyols and isocyanates. As well as MDI, toluene di-isocyanate (TDI) may be used. The combination of isocyanate and polyols is often supplied as a 'system', particularly to medium or smaller users. There is therefore a strong element of application design and technical service in this business.

ICI is the only company producing nitrobenzene and aniline in the UK. Other West European producers are Bayer, BASF, Dow and Anilina de Portugal. The total West European production in 1997 was around one million tons of nitrobenzene and 0.75 million tons of aniline. With its new capacity at Wilton, ICI will be a leading player in Europe. Most of these producers, including ICI, are integrated downstream into MDI and participate in the polyurethane business. Several producers ship aniline between countries. ICI will export to its Rozenburg facility in the Netherlands, for example.

Recent years have seen substantial expansions or new capacity in the chain to MDI. Although the demand for polyurethane and MDI continues to grow healthily, the capacity increases are such that it is likely that the West European producers will have to export some of their production.

6.7.2 Industry economics

As with most commodity products, the pricing of aniline for sales between companies is related to the cash cost of production, plus a margin that varies with the balance of supply and demand. On Table 6.21, indicative cash costs of production for nitrobenzene and aniline in Western Europe are given. The costs are calculated taking into account the specific circumstances and unit costs of five selected sites. The nitrobenzene is transferred to the aniline plant at a value related to its cash cost at the site.

Table 6.21 Cash costs of production for nitrobenzene and aniline, typical, Western Europe, 1997 prices

	Low cash cost (£/ton)	High cash cost (£/ton)
Nitrobenzene	170	195
Aniline	270	320

The cash cost margin on aniline, based on merchant prices, is around £110 to £180 per ton. The value at which material is transferred within a company may be more closely related to the cash cost, as noted above.

6.7.3 Costs of abatement

Nitrobenzene/aniline is included as a process case because of the specific requirements associated with strong aqueous effluents from nitrobenzene production, as described in Section 5.6. There are other pollution control requirements, such as scrubbing of NOx, but the purpose of this section is to present typical costs of strong effluent treatment in the context of production economics.

Table 6.22 shows the approximate cost per ton of aniline for three methods of disposal: thermal oxidation, wet air oxidation, and deep welling, as practised in some plants in the United States. Economics are based on 200 000 ton per year aniline. The cost of thermal oxidation assumes that fuel is at the price of external purchase. If the fuel is a process stream that could not be beneficially used elsewhere for technical or regulatory reasons, the cost would be reduced substantially.

Table 6.22 Cost of treatment of nitrobenzene strong effluent

Technique	**Cost per ton Aniline** (£ per ton)
Deep well	1
Thermal oxidation	12
Wet air oxidation	4

Within the context of the economics of the business, the costs of effluent control are certainly significant. However, with all West European plants being required to adopt similar measures, and recognising the place of nitrobenzene/aniline in the polyurethane business, the cost is not of a devastating magnitude. This assumes, as elsewhere in Section 6, that this is a single requirement and that similar expenditure would *not* be expected after a four year period.

6.8 Sectoral Affordability

It is clear from the process cases reviewed in Sections 6.2 to 6.7 that it is not possible to define affordability in a way that applies across the full petrochemical and large volume organic compound sector. The following notes give directional comment.

Many of the products in this sector are commodity materials. Price is a very important factor in competition, which is often on a regional or even global basis. Additional net costs, relating to pollution abatement, will affect the producer's margin rather than being passed on to customers for these products.

Another important characteristic of the sector is that, for many products, the business is heavily cyclical. This has implications for Inspectors in determining whether measures are affordable in the context of industry economics. Firstly, it is not meaningful to quote environmental costs as a percentage of margin or profit for a single year; averaging across the business cycle is needed. Secondly, the industry may suffer a cash shortage or even a cash drain at some times in the business cycle. This may influence any deadlines set for implementation of improvements.

With competition on an international basis, the profitability of the UK sector depends on the cost position of producers in other countries. Important elements of that cost position include feedstock type and source, energy costs, and plant size. The competitive position of the UK opposite other EU countries varies between different products. In general, however, the position that UK industry can afford abatement techniques that are applied in other EU countries could be taken as a first starting point. In some cases, producers may be able to highlight systematic differences between the UK industry and that in other EU countries.

There are instances where Western Europe as a region is vulnerable to cost competition from other regions, in either the domestic market or in exports, such as to Asia. The Arabian Gulf and the United States have cost advantages for several commodity petrochemical products, for example. The West European margins for some products may therefore be below the level at which reinvestment is justified. As it is not possible to generalise across the sector, individual producers would need to demonstrate to Inspectors where they believe margins to be particularly hard pressed.

There are two main elements to additional costs of abatement: capital expenditure and annualised costs. The capital expenditure of operating companies in this sector varies from year to year. Capital investments in new plant tend to be large and occasional. From examination of annual reports, it appears that a typical continuing level of capital expenditure is one to three percent of gross revenue. When major investments or restructuring are occurring, this could rise to 10-20 percent of revenue.

Annual environmental costs, when quoted by companies, typically amount to around one to two percent of revenue.

These very approximate indicators may be of assistance to Inspectors in putting additional abatement costs into an economic context.

All the costs of abatement in this report are calculated taking as an assumption a lifetime of ten years. If companies are required to introduce abatement measures in a shorter time period then the costs (as calculated) would accumulate. This should be taken into account in calculations of economic impact of abatement measures.