PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Cleaner technology: more from less

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Cleaner technology: more from less

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Process technology in the chemical industry has long been focused on safe, efficient manufacture of new chemical entities to provide society with better food, shelter, clothing, healthcare, communications, etc. Competitive economics has ensured cost-effective use of capital and raw material resources while regulation has set standards to protect the public from harmful releases and other unacceptable degradation of the environment. This paper examines several holistic approaches used to secure an integrated management response to meet market needs. Criteria for the development and worldwide deployment of technology are discussed and some measures and indicators of performance are developed to help set priorities and measure environmental progress.

1. Introduction

The chemical industry has, for decades, been driven to search for new products which meet societies' needs for better goods which are life enhancing and reduce the hazards and drudgery of primitive living. When these new products emerged, e.g. plastics, synthetic fibres, refrigerants, pharmaceuticals, agrochemicals, it was only a short time before market and legislative pressures ensured that the products were manufactured by efficient processes which had regard for use of costly resources, safety of the public and employees and increasingly, latterly, protection of the environment. Sophisticated regulatory regimes controlling safe use of products and design and operation of chemical manufacturing processes to ensure no harm to the environment developed rapidly in Europe and North America and quickly spread to fast-developing countries in Asia–Pacific. For process technology the major regulatory thrust has been towards application of best available technology (BAT). Application of BAT regardless of local geography, infrastructure and intended use for the environment, e.g. industrial use versus freshwater trout fishery can put unbearable financial pressure on industry for minor environmental gain. A more pragmatic approach to securing desired environmental quality standards (EQS) has found greater favour in conjunction with use of BAT. In parallel with this the chemical industry has taken an active role in developing new methodology for assessing the comparative potential environmental impacts of its products and processes. This has created substantial life-cycle assessment databases for many staple products of the chemical industry which can be used for eco-labelling assessments. Building on its large investment in quality management systems the industry has embraced environmental management systems as a framework for rigorous attention to environmental issues and as a vehicle for continual environmental performance improvement, in particular

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Table 1. *Problem: PTA offgas treatment*
(For greater than 100 t h^{-1} of waste gases.)

	level	required standard
CO	4500	100 ppm
hydrocarbons	600	80 ppm

technology:
catalytic combustion

$$CO + HCs + O_2 \xrightarrow{\text{catalyst}} CO_2 + H_2O$$

through the clarity of responsibilities, standards required and reporting explicit in a recognized EMS. Environmental issues achieved business prominence in the USA as a result of liabilities for contaminated land inherited from past operations whose waste disposal standards fell far short of those required today. This has elevated environmental issues on the agendas of shareholders, bankers and insurers to the extent that shareholder value has now acquired an environmental context in part due to past liabilities but also in the sense of an enterprise's capacity to manage environmental risks associated with its products, its processes and other services. The main body of my paper sets out examples of how ICI has responded to a range of different environmental challenges to its businesses.

2. Reduced emissions from PTA manufacture

ICI has produced pure terephthalic acid (PTA) for polyester since 1967 when it first commissioned a 36 000 tonnes per annum plant at Wilton, UK. Today, we produce close to one million tonnes worldwide and our capacity is growing to meet increasing demand. A major challenge in PTA technology is the need to deliver world class environmental performance while simultaneously achieving substantial reductions in both variable and capital costs. This task is particularly acute in the area of treatment of spent air (offgas). A world scale PTA plant uses 150 000 m^3 h^{-1} of air, which after reaction, is discharged to the atmosphere. It contains carbon monoxide (CO) and volatile organics (VOCs) (table 1). Older plants discharged this 'offgas' following condensation and scrubbing of VOCs. More recent plants used, in addition, end of pipe catalytic combustion to achieve partial removal of CO (60%). A review showed that current and expected emissions standards were, or would be, similar throughout the world, and that extensive treatment of the offgas was essential for future investment.

The challenge was to meet this environmental performance in the context of the overall project targets of capital cost reduction and improvement in variable costs and a project team was set up to look at the means of achieving this. The need to maximize capital productivity led to the need to integrate any catalytic combustion unit (CCU) into the core process, using the combustion to preheat gas into the offgas expander.

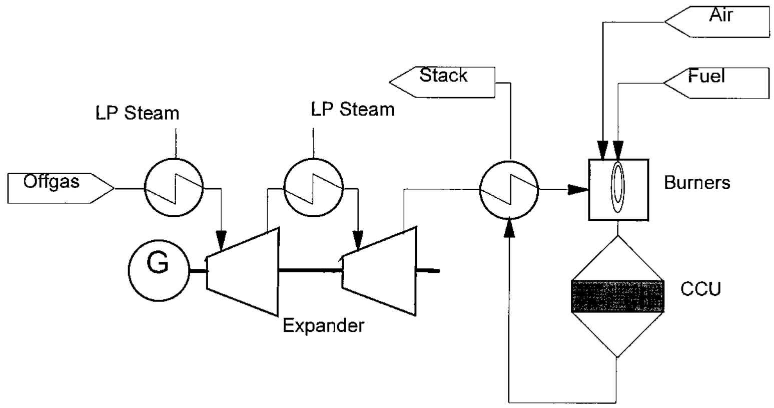

Figure 1. Existing plant: the offgas, at pressure, is heated and power is recovered by letting down to atmosphere through an expander: the catalytic combustion unit (CCU) operates at low pressure in the expander exhaust.

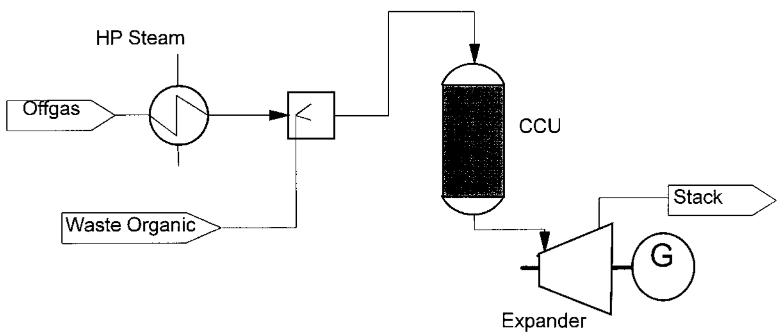

Figure 2. New design: the CCU is moved to upstream of the expander. The heat of combustion, instead of being wasted, raises the expander inlet temperature and this energy is recovered as power, at high efficiency. This heat does not provide all of the temperature rise required, so that additional heating is needed. The CCU operates at high pressure and exit temperature. Various options were explored. A novel scheme to use injection of fuel directly into the process stream was shown to be the most attractive, particularly as this enabled use of an organic by-product stream (recovered in the distillation area of the plant) as a fuel source.

Table 2. *Benefits*

(Compared to the design used in existing plant, the technology achieves world standard environmental performance by reducing CO discharge by 95%. Capital costs are reduced by 25% and substantial reductions in variable costs are achieved.)

	existing	new
environmental performance (CO)	2000 ppm	100 ppm
capital cost (%)	100	75
nett operating gain	—	substantial

3. Paints VOCs reduction

Most batch processes which use organic chemicals will result in the release of volatile organic compounds (VOCs) to the atmosphere. VOCs produce photochem-

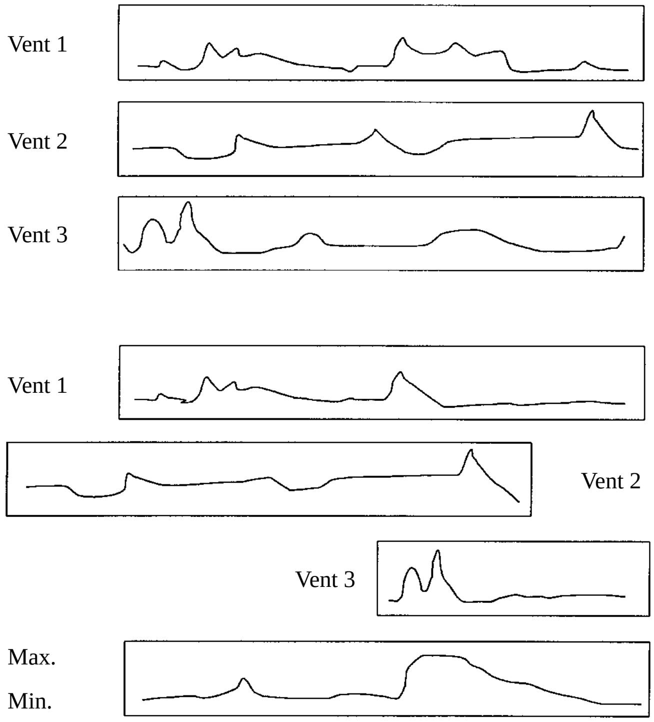

Figure 3. Worst-case maesurements.

ical oxidants in reaction with oxides of nitrogen in the presence of sunlight and so VOC emissions are now regulated in most European countries. My next example describes how ICI Paints has employed a simple approach to analysing VOC emissions prior to implementing source reduction or recycling techniques which meet regulatory requirements while avoiding the need to install expensive offgas incinerators, particularly on paint resin plants where they are a potential safety hazard. Batch processes can be very difficult because flows, concentrations and compositions change throughout the process and between products made on the same plant. ICI Paints have measured and modelled VOC emissions to establish a database of batch profiles (figure 3). A range of process and engineering options are then considered. In one case study a resin operation which produces coatings for the packaging industry was found to have VOC emissions at worst 46 kg h^{-1} (figure 4) because an extraction system above four mixers where hot resin was blended with solvents ran continuously. The regulations required abatement techniques above 2 kg h^{-1}.

The mixing tanks were fitted with sealed lids, a vent pipe and condenser were installed with lip extraction round a manhole and emissions were reduced by 40 kg h^{-1}. After completing engineering work on a number of vents on the site the worst case produced a peak emission of 1.6 kg h^{-1}. The authorities are satisfied with this approach and the resulting improvement in emissions.

4. Paints waste solid and liquid reduction

Typically in 1989 a paints plant which produced 100 million litres of product per annum generated six million litres of dry waste for landfill, five million litres

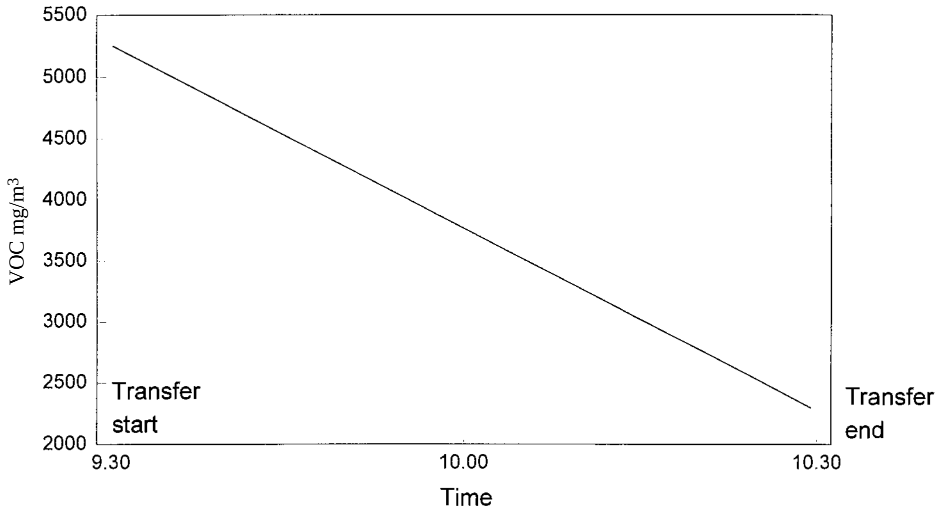

Figure 4. Finish tank extraction—phenolic resin.

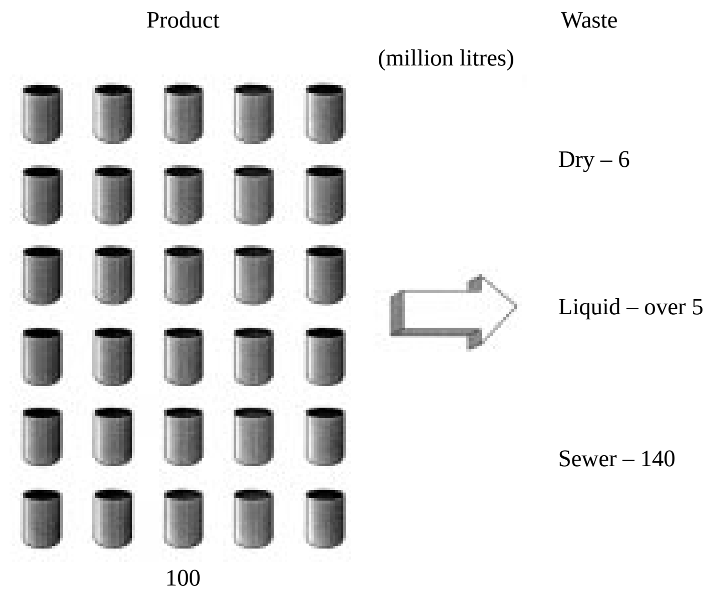

Figure 5. Typical paint plant 1989.

of liquid waste and 140 million litres of waste water for treatment (figure 5). Total waste disposal costs were over £500 000 per annum. ICI Paints Europe addressed each of these streams with a vigorous waste minimization programme and achieved the ICI objective of 50% waste reduction on 1990 base well ahead of the 1995 target (figure 6). In particular on the 'white' emulsion paint plant (figure 7) some three million litres per year of waste washwaters were generated from cleaning vessels and presented a major disposal problem. The waste minimization programme enabled: (1) high speed dispersers were washed into the mixers which removed an effluent stream and saved millbase; (2) batches were scheduled to minimize the need to wash between colours and whites; (3) an ultrafiltration plant has been installed at a cost

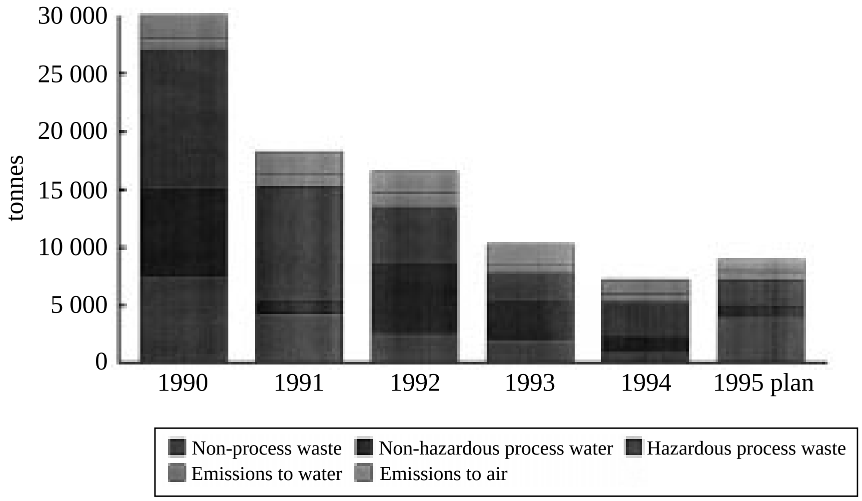

Figure 6. Paints European wastes 1994.

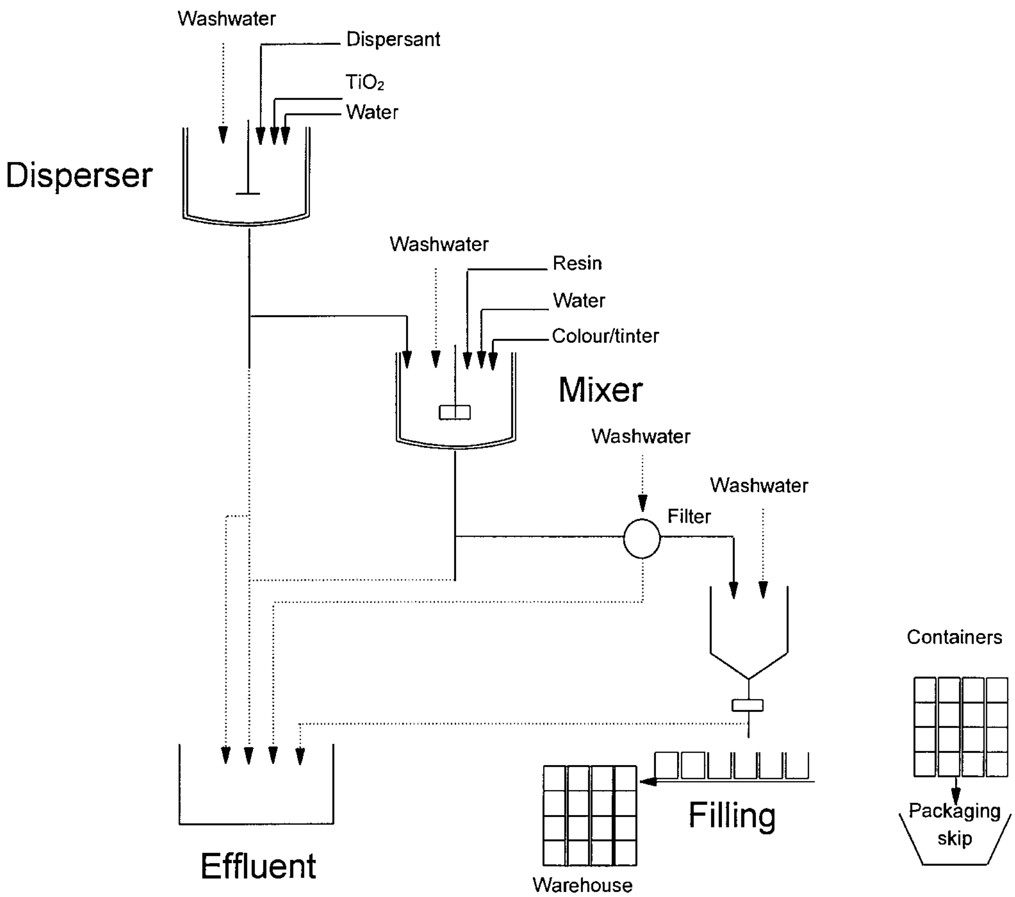

Figure 7. Water-based bulk white paint.

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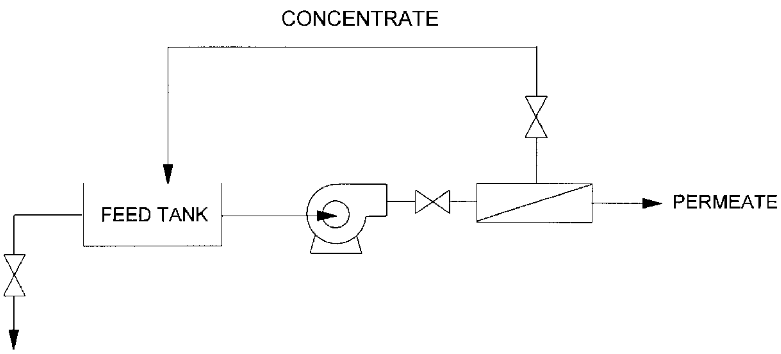

Figure 8. Ultrafiltration batch system.

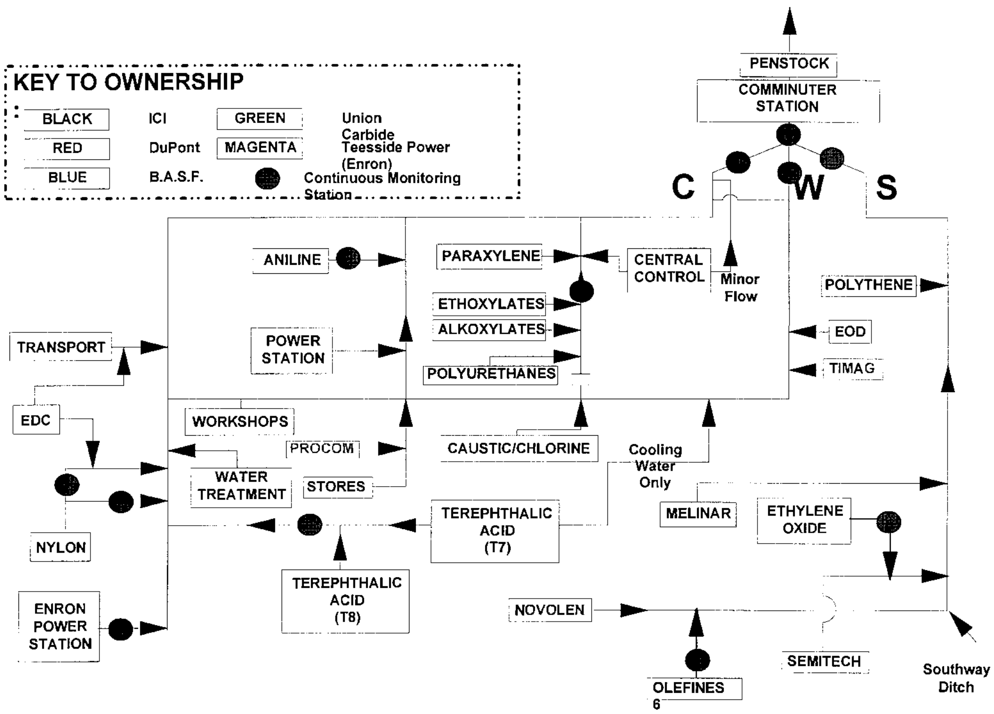

Figure 9. Schematic diagram of Wilton site drainage system.

of around £650k (figure 8) to recover valuable paint from the remaining washings, return the recovered water for cleaning use and thus significantly reduce waste. Solid waste has been virtually eliminated from the plant.

5. Reduction of chloroform in wastewater

An important example of chemical detection work has been undertaken in no lesser place than the ICI Wilton site wastewater drains (figure 9). By any standards this is a complex system serving one of the largest collections of chemical plant in Europe. The problem the site faced in 1992 was a requirement by the National Rivers Authority to reduce the amount of chloroform in the River Tees to meet an environmental quality standard (EQS) of 12 $\mu g\,l^{-1}$. Achievement of this level required a major effort by

Table 3. *Identification of chloroform formation mechanism*

most likely mechanism is the haloform reaction

$$RCOCH_3 + 3OCl^- = RCOO^- + CHCl_3 + 2HO^-$$

—favoured by strongly alkaline conditions

—specific
—for $RCOCH_3$ or precursors
—to give chloroform but not mono-and dichlormethanes

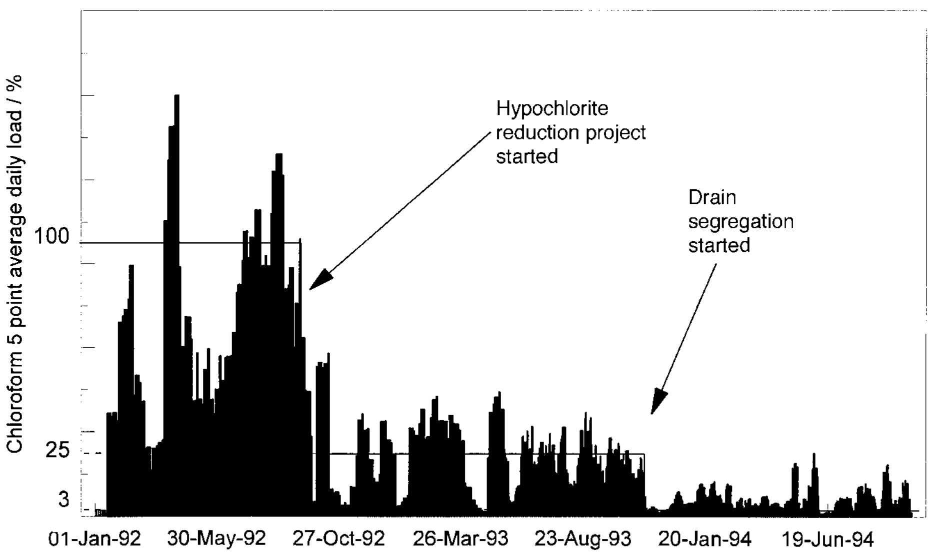

Figure 10. Wilton site chloroform emissions.

site personnel to track down the source of about 200 kg day^{-1} chloroform which was appearing in a daily outfall of some 120 000 tonnes of wastewater and then reduce the quantity to meet EQS requirements.

The source of chloroform was attributed to a haloform reaction taking place in the drains (table 3) between sodium hypochlorite and acetaldehyde at very low concentrations, high pH and ambient temperature.

A major programme was undertaken to reduce hypochlorite emissions in 1993 by installation of a catalytic unit which broke down the waste bleach to salt and oxygen. These reductions effected a step change reduction in chloroform from October 1992 (figure 10) but the improvement was insufficient to meet the River Tees EQS target. In October 1993 the further step of segregation of the wastewater streams containing chlorine and carbon source was taken and efforts were made to ensure these streams did not meet under high pH or indeed low pH conditions. This segregation system is providing an interim solution to achieve the required EQS and has provided time to investigate a long term cure to this problem.

6. Dust-free drying

Spray drying is an everyday way of turning a solution or slurry into a free-flowing powder, by spraying it into the top of a counter-current flow of hot gas. The downside

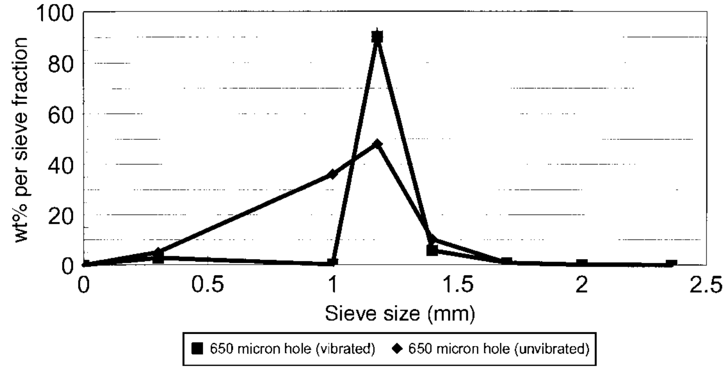

Figure 11. Prilling: size distribution results.

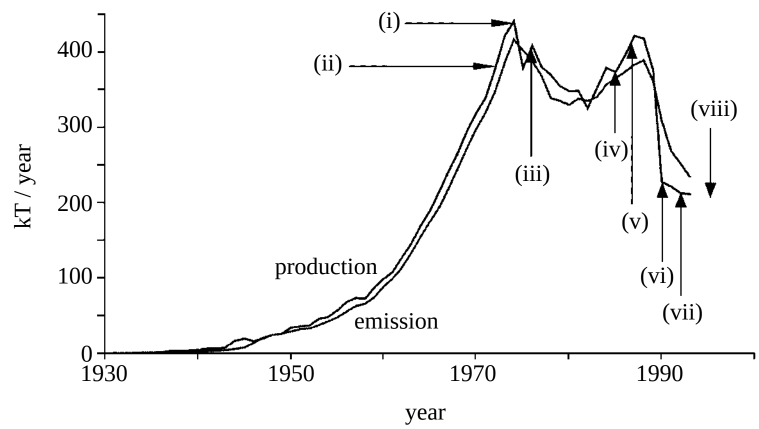

Figure 12. CFC 12 global production and emission: (i) 1974, Rowland & Molina's theory published; (ii) 1972, industry funds analyses for CFCs in air. Fluorocarbon panel formed; (iii) 1976, 'ban' on CFCs in aerosols in USA; (iv) 1985, Antarctic ozone hole; (v) 1987, Montreal Protocol 50% cutback; (vi) 1990, London Amendment phaseout by 2000; (vii) 1992, Copenhagen Amendment phaseout 1996 and controls on HCFCs; (viii) 1995, Vienna.

is that it also makes dust, between 5 and 2 5% of the product, which usually is unacceptable to the customer and must be reprocessed. ICI Engineering set out to gain a more fundamental understanding of how these fluids, often non-newtonian, behave as they are atomized and undergo evaporation. They engaged interface physics and aerodynamics. A crucial factor was to maintain a uniform size of droplet. The outcome is a way of keeping the particle size within much narrower limits (figure 11), almost free from dust, of use in making ceramics, paints, propellents, catalysts and gas generators for airbags.

7. The development of Klea 134A production technology

In 1990 ICI became the first company to open a commercial scale plant for refrigerant R-134a (now marketed as Klea 134a), a leading alternative to the CFCs implicated in depletion of the Earth's ozone layer. The 1987 Montreal Protocol was the first international treaty to address a truly global environmental problem (figure 12) and it was further strengthened in both 1990 and 1992 to a CFC production phaseout by 1996.

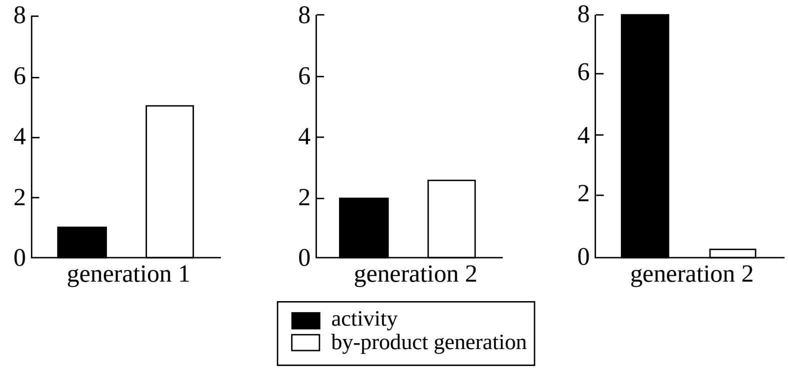

Figure 13. Klea 134a catalyst development. Improvements in activity and sel ectivity.

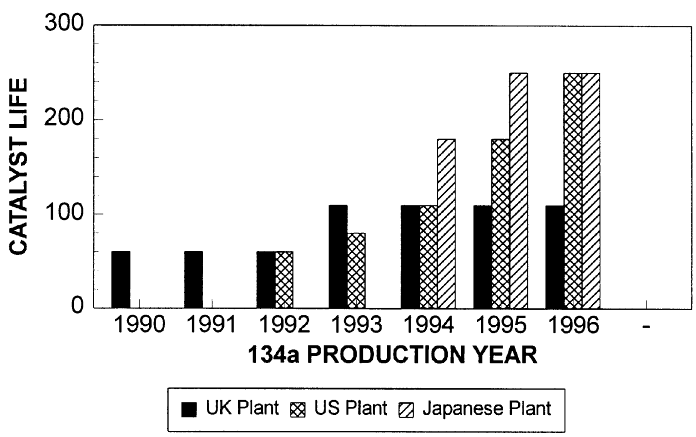

Figure 14. Klea 134 catalyst development.

In 1987 ICI established a multi-disciplinary team to develop a safe and efficient process for making Klea 134a and by 1993 commercial scale plants were operational at Runcorn, UK; St Gabriel, Louisana USA; and Mihara, Japan. The manufacturing process involved catalytic two stage reaction of trichloroethylene (TRI) with hydrogen fluoride (HF) gas.

$$\begin{array}{lll}(1) & \mathrm{TRI} + \mathrm{HF} & \longrightarrow \; 133\mathrm{a} + \mathrm{HCl} + \mathrm{heat},\\ (2) & 133\mathrm{a} + \mathrm{HF} + \mathrm{heat} & \longrightarrow \; 134\mathrm{a} + \mathrm{HCl}.\end{array}$$

A great deal of innovative chemistry and engineering was devoted to the project, in particular enabling faster reaction at lower temperature, removal of water from corrosive hot wet gases to protect the plant materials of construction, and to novel distillation techniques to separate out pure product and recylce unreacted ingredients to the reactors. Catalyst development was cruical to securing effective conversion of raw materials to pure Klea 134a. Through improvements in catalyst activity and selectivity (figure 13) coupled with extension in catalyst life (figure 14) the capacity and efficiency of the plants has been increased many fold—without the need to invest large amounts of capital in additional new plants. The development of Klea 134a production technology was honoured with the MacRobert award by the Royal Academy of Engineering in 1993.

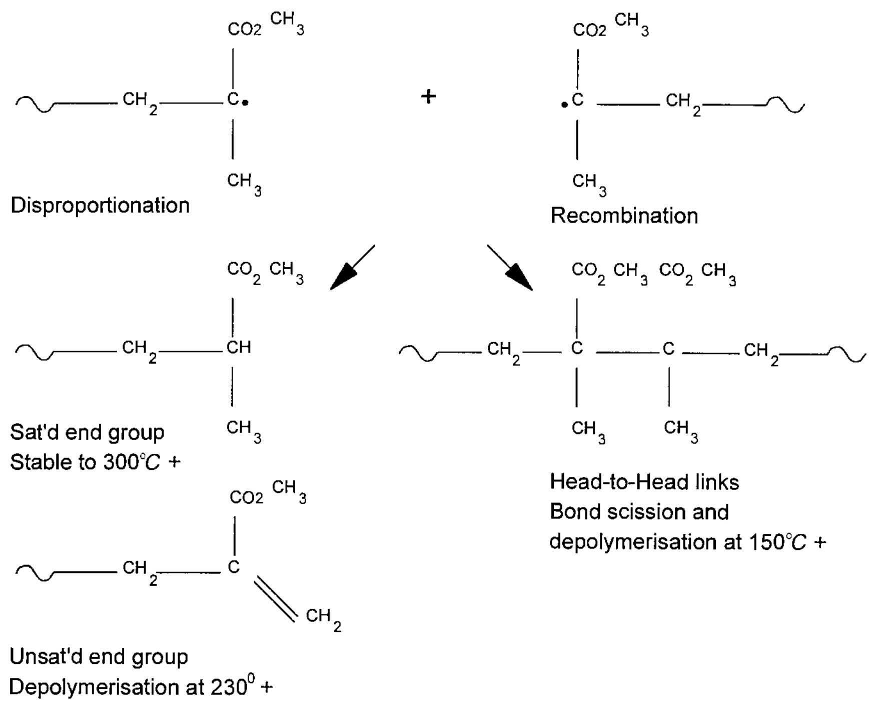

Figure 15. Thermal degradation of PMMA.

8. Acrylics waste recycling

My final example of the application of chemical process technology addresses a difficult plastics recycling issue. It is now becoming clear that there are a number of problems—environmental, technical and economic—associated with the recycling of small volume mixed and contaminated plastic waste. Typical problems are as follows. (1) Economic: cost of sorting, collecting, washing—economies of scale. (2) Environmental: energy used in sorting, washing, melting and reprocessing can exceed energy saved by recycling. (3) Technical: downgrading of plastic (physical properties suffer) and recycled content (amount of material which can be incorporated into virgin product). However, we have found that with acrylic materials we can avoid any of the above problems by giving some modest attention to the logistics of return of materials after use.

(*a*) *Acrylics: designed for recycling*

Chemical recycling is the most sensible method for recycling. It is characterized by high recovery efficiencies yielding high value products when compared to mechanical recycling, i.e. melting and/or grinding of thermoplastics to produce lower quality products—downgraded and with limited recycled content. Closed loop recycling is the most efficient form of recycling—direct savings of resources (both material and energy) versus virgin product. ICI Acrylics are doing both! ICI has been recovering methyl methacrylate (MMA) monomer by thermal depolymerization since the 1940s and this material is repolymerized yielding virgin quality polymer. The origins of the thermal instability lie in the mechanism which terminated the free radical polymerization (figure 15).

Polymethyhmethacrylate (PMMA) manufacture was established in the 1930s and

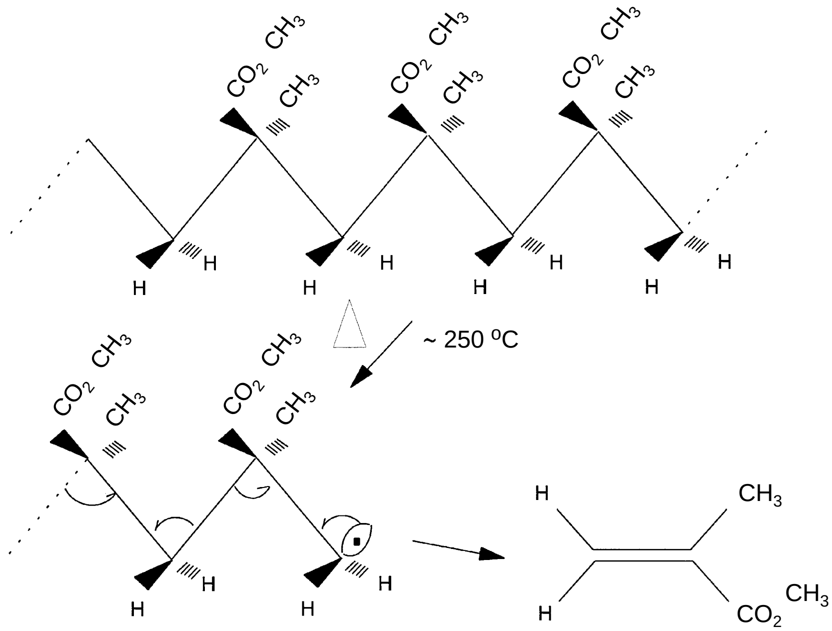

Figure 16. 'Unzipping' of poly(methylmethacrylate).

first produced commercially at Billingham in two product forms: Perspex®—cast sheet by bulk polymerization; Diakon®—moulding powder by suspension polymerization. The unique PMMA properties of optical clarity, weatherability, colour and durability led to use of injection moulded, dyed Diakon® for automotive rearlights. Melt extrusion of Perspex® sheet thermoformed it into lighting diffusers and skylights. PMMA sheet offcuts, recovered automotive parts, redundant signage, etc., can be segregated and returned to a recovery point by simple logistics. MAA can be recovered from this waste by a thermal depolymerization process (figure 16). The monomer is suitable for repolymerization to PMMA with properties indistinguishable from virgin polymer.

9. Delivering environmental performance

Converting innovation to performance requires painstaking and unrelenting management effort. In common with most major manufacturers ICI embraced the rigorous application of total quality management through ISO 9000 certification and then built on this experience with an integrated safety, health and environment (SHE) management system (figure 17). ICI had already adopted 19 mandatory standards worldwide (table 4) before certification to BS 7750, EMAS or ISO 14001 became available and the Company requirements have since been reviewed to ensure they cover all the relevant international standards requirements.

One special feature of the ICI SHE MS is the obligation on constituent business to produce an annual letter of assurance to the ICI executive director responsible for SHE setting forth the level of compliance with company SHE standards and incorporating plans to address those areas where further improvement is needed. These processes have been aided by the development of metrics to assess environmental performance. In the late 1980s simple measures of regulatory compliance were es-

Figure 17. The ICI group SHE management system.

Table 4. *The ICI group SHE standards*

1 safety, health and environmental (SHE) commitment	10 systems of work
	11 emergency planning
2 management and resources	12 contractors and suppliers
3 communication and consultation	13 environmental impact assessment
4 training	14 resource conservation
5 material hazards	15 waste management
6 acquisitions and divestments	16 soil and groundwater protection
7 new plant, equipment and process design	17 product stewardship
8 modifications and changes	18 SHE performance and reporting
9 SHE assurance	19 auditing

tablished together with reporting of spillages, in various levels of seriousness and complaints ranging from simple nuisance issues through to environmental infringement prosecutions. Further major steps forward in 1990 set improvement objectives for the organisation which included: worldwide environmental design standards for all new plant; 50% reduction in waste, particularly hazardous waste; substantial improvement in energy efficiency; commitment to recycling both in-house and in conjunction with customers.

10. Future challenges

In October 1995 ICI announced its SHE Challenge 2000 programme which set out improvement targets in environmental performance together with new safety

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

and health programmes. The environment targets built on previous experience but included a more focused approach towards the reduction of emissions (reduction of environmental burden). The objectives of the new approach were: to compare the significance of site emissions better (not just aggregate tonnes); to help set priorities for improvement plans; to help communicate performance progress. The programme supports 'responsible care for the environment'—one of the six core values embraced and recently published by ICI. The methodology relates individual substance emissions to important environmental categories such as global warming, acidification, ecotoxicity, etc., it then weights the contribution of each substance emission to its category (or categories) according to scientifically based factors, e.g. global warming potential (GWP) versus CO_2, acidity in tonnes H^+ ecotoxicity related to Environmental Quality Standard (EQS). The burden data can then be aggregated under the different environmental categories or parameters at site, worldwide business or ICI group level to help set priorities and display progress. No attempt will be made to aggregate across the parameters, e.g. global warming and ozone depletion because the units of measurement are totally different. Detailed development of the methodology is in hand. It will be subject to peer review by leading academics in the field prior to being made available publicly. This work is in support of the ICI SHE Challenge 2000 target, 'we will halve the environmental burden of our operations worldwide across a range of specific environmental parameters namely ecotoxicity, aquatic oxygen demand, acidity and potentially hazardous emissions to air using 1995 as the baseline'. Application of process technology to improve environmental performance of operations will be complemented by a major drive on product stewardship to support responsible design, transportation, use and disposal of chemical products. Achieving these challenges will be one of our main contributions to the worldwide chemical industries 'Responsible Care' initiative.

I acknowledge the work of many scientists and engineers throughout ICI who made this paper possible.