Department of the Environment

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Review of Operational & Experimental Techniques for the Removal of Bacteria, Viruses & Pathogens from Sewage Effluents

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APPENDIX I

Reference WR/7/4/26 and
PECD/7/7/260

Mr Healey	Rm B4.46 RH	
Dr Otter	Rm A4.18 RH	
Mr A H Goodman	Rm B4.55 RH (OR)	(minute only)
Mr Hydes	Rm A4.44 RH	
Mr Rodda	Rm A4.33 RH	
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Dr Simpson	Rm A4.10 RH	} Please share
Mr Worthington	Rm A4.12 RH	
Dr Adams	Rm A4.20 RH	
Mr Mills	Rm A4.37 RH	(minute only)

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Dr Otter has accepted the final report on this project. The contract was awarded after a competitive tender exercise. In the event this Department accepted the third lowest tender, that from CES Ltd. Herewith your copy of the final report.

Mr Mills should now begin a Value-for-Money exercise please.

K D P CLOSE
Rm AG.25 RH
X 8695

31 October 1988

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Executive Summary

EXECUTIVE SUMMARY

Pressure for compliance with the EEC Bathing Water Quality Directive has prompted investigation into methods of disinfection for marine discharge of wastewater. Disinfection may be an alternative to discharge through long sea outfalls or may provide a temporary solution while outfalls are constructed. Chlorination is the established disinfectant for both water (eg. UK) and wastewater (eg. US), but increasing concern over its environmental impact has led to development of alternatives including UV; ozone; lime; peracetic acid; chlorine dioxide; bromine chloride and gamma irradiation.

The Department of the Environment commissioned CES to undertake a comparative evaluation of disinfection techniques. The objectives of the study were to review both current operational techniques and experimental techniques for the inactivation of bacteria, viruses and pathogens in sewage effluents, with particular reference to marine discharges. The inactivation efficiency of the various techniques was to be compared and the actual or potential capital and operating costs evaluated. In addition, promising techniques for future application and aspects of disinfection requiring further research were to be identified.

The report covers firstly the properties of individual operational or experimental disinfectants, reviewing their production and application; chemistry; mechanism of disinfection; inactivation efficiencies; factors affecting efficiency; and environmental impact. Operational and cost data from pilot and full scale trials, both reported in the literature and provided by UK Water Authorities are presented. Subsequent sections of the report comprise a cross comparison of disinfectant alternatives in terms of their inactivation efficiency, environmental impact and cost; and a brief summary of Water Authority attitudes to disinfection. Factors affecting the choice of disinfectant have been discussed and areas for future research identified.

a) Operational disinfection systems

* **Chlorine** is the most widely used wastewater disinfectant; in the US approximately 62% of total municipal wastewater is chlorinated. Chlorine is applied either as elemental chlorine (a dense corrosive gas), or as a hypochlorite compound (typically sodium hypochlorite solution) supplied as a 14-15% solution or generated on-site from brine or seawater using electrolysis (OSEC). Hazards associated with the handling of chlorine gas makes the use of sodium hypochlorite solution or OSEC preferable in densely-populated areas.

Chlorine reacts rapidly with ammonia and organic compounds to form chloramines and chlorinated organics. High concentrations of ammonia in wastewater give combined chlorine residuals. Despite a much slower bactericidal activity than free chlorine, given sufficient contact time, chloramines are equally effective

disinfectants. However, both free and combined chlorine show low inactivation efficiency for resistant microorganisms such as bacterial spores and cysts.

Chlorine residuals (both free and combined) are acutely toxic to aquatic organisms at low concentrations and are persistent due to their stability. The US EPA has proposed stringent discharge requirements for total residual chlorine (mean $7.4ugl^{-1}$ for saltwater); dechlorination is necessary at many chlorination facilities. Certain chlorinated by-products, eg. trihalomethanes (THMs) are carcinogenic and there are significant adverse environmental effects associated with chlorinated organics formed during wastewater disinfection.

Despite its disadvantages, chlorine remains one of the most cost-effective disinfectants available with low capital and operating costs of under $2pm^{-3}$. It is also suitable for application to raw sewage, unlike ozone and UV. Its ease of application makes it suitable for emergency disinfection or as a temporary measure.

* **Chlorination/dechlorination** was used at over 5000 wastewater disinfection plants in 1987. The two most common dechlorination processes use sulphur dioxide or granular activated carbon (GAC), though sodium bisulphite, sodium sulphite, sodium thiosulphate, sodium metabisulphite and biotin may also be used. Sulphur dioxide gas requires similar dosing equipment as chlorine and reacts with chlorine residuals on an equal molar basis (approximately $1mgl^{-1}$ is required to remove $1mgl^{-1}$ chlorine). A disadvantage is that excessive dosage of sulphur dioxide leads to depression in pH and dissolved oxygen, necessitating reaeration. The total cost of chlorination can be increased by up to 30-50% with the addition of a dechlorination step. Dechlorination has been shown to reduce both chlorine residuals and the mutagenic activity of water. GAC dechlorination can reduce mutagenicity in drinking water both by application before (removal of precursors) and after (removal of organochlorine compounds) chlorination.

* **Ozone** is being used increasingly for wastewater disinfection in the US and to a lesser extent in Europe. In 1987 there were 19 operational plants in the US and 2 small scale wastewater plants in France. Ozone is an unstable gas which is generated on site by electrical discharge through air or oxygen. It decomposes rapidly in aqueous solution and under alkaline conditions hydrolyses to form the $OH\cdot$ radical, which is a powerful oxidant. Conditions for oxidation are improved in acidic pH, through slower direct oxidation. Ozone is both an efficient bactericide and virucide, characterised by its rapidity and the low concentrations required. Typical ozone doses in practice for secondary effluents are 10 mgl^{-1} for a contact time of 10 min.

Ozonation is currently only practicable on effluents treated to at least secondary quality. Ozonation of lower quality effluents is limited by the high ozone demand associated with high COD and SS levels. One advantage over chlorine is that ammonia levels in wastewater have little effect on disinfection efficiency. Though ozone appears not to produce THMs and may even destroy a number of THM precursors, it oxidises a wide range of natural organics in wastewater and can lead to significant changes in the nature and concentrations of certain organic compounds. Ozone destroys most of the non-volatile organic constituents in wastewater but produces others; concentrations of mutagenic micropollutants can be increased by ozonation.

Though highly toxic, the hazards from ozone are minimised because it is utilised immediately. However, operators need protection by adequate leak detectors as concentrations of ozone generated are in excess of occupational exposure limits. Accident risks at ozonation plants are low; in over 70 years of large scale disinfection of potable water in Canada and Mexico no fatalities have been reported. Costs are largely generating equipment costs and the energy costs involved in ozone production; approximately 30% of total costs arise from amortisation of capital and 17% from power consumption. Comparison of operational wastewater disinfection plants in 1984 found that capital and operating costs for ozonation were approximately 2.5 and 2 times those of chlorination/dechlorination respectively.

* **Ultra-violet (UV)** disinfection systems were operating at 53 wastewater plants in the US and Canada in 1984, with 64 in the design or construction phase. These facilities operate sucessfully on secondary effluents with flow capacities from $2.7m^3d^{-1}$ - $2.2m^3s^{-1}$. Wastewater quality is a major limiting factor because high concentrations of solids can absorb UV and protect microorganisms by encapsulation. Secondary treatment is necessary for UV to be both technically and economically feasible. Factors governing the efficiency of disinfection are UV dose (a product of lamp intensity and contact time) and wastewater quality. Typical operational dosages for secondary effluents range from 30 to 50 $mWs\ cm^{-2}$. Inactivation of viruses requires 3-4 times the dose for bacteria, whilst bacterial spores and cysts are up to 9 and 15 times more resistant. Comparison of UV dose with chemical dosages is difficult but the range of UV doses for different pathogens appears narrower than that of chlorine. It is a more efficient virucide than chlorine.

An advantage of UV irradiation is that it produces no harmful by-products and causes only slight chemical changes in non-volatile organics in wastewaters. UV does not produce a lasting residual thus there is no residual toxicity to marine organisms. There is no economy of scale for UV because the effluent flow rate is proportional to the number of lamps. The major capital outlay is for UV lamps, while operational costs arise from lamp replacement and electricity consumption. Capital costs tend to be higher than those of a dechlorination plant whilst operating costs are of the same order of magnitude.

- The **Clariflow** single-stage lime treatment process was developed in the UK by Blue Circle Industries plc in conjunction with Southern Water and Portsmouth Polytechnic. The first plant has been in operation at Sandown, Isle of Wight, since 1985 and successfully treats up to 21,000m^3d^{-1} of raw, screened sewage. A patented lime-based slurry facilitates the production of an upflow sludge blanket. A minimum pH of 10.5-11.0 is required to achieve adequate coliform disinfection, although at lower pH improved removals of BOD, SS and metals are observed. A high pH regime has been shown elsewhere to be effective for inactivation of other pathogenic microorganisms including viruses.

  The effluent is necessarily of a high pH, which may have a localised ecological impact at the site of discharge. The process also generates a large volume of sludge which must be dewatered and disposed of either to agricultural land or, as at Sandown, to landfill. Capital costs are high, although these may decrease for subsequent plants. Operating costs are high, typically 5 times those of chlorine. Costs rise disproportionately with pH, therefore it has been suggested that a lower pH regime may be operated in winter when bacterial quality is less critical.

b) Experimental disinfection systems

- **Chlorine dioxide** has had extensive use as a water disinfectant in Europe and the US but has yet to be used as a wastewater disinfectant. It is both a powerful bactericide and virucide even at high pH levels and has an important advantage over chlorine in that it does not appear to produce THMs.

  Chlorine dioxide is a yellow explosive gas produced *in situ* from the reaction of sodium chlorite with either chlorine gas or hydrochloric acid. Even when generated on site there are hazards involved in chemical handling, although development of a new method of production under vacuum eliminates the explosive hazard. Chlorine dioxide is a more powerful oxidant than chlorine and is also a more effective virucide. Use of indicator organisms may thus yield conservative performance data for its disinfection of secondary effluent. Chlorine dioxide dosages of 0.05-1.0 times and residuals of 0.3-0.1 times that of chlorine achieve equivalent bacterial reductions.

  Though THMs are not formed, chlorine dioxide can react with organics to yield other potentially hazardous chlorinated or unchlorinated by-products, some of which are known carcinogens. Potential environmental impacts on marine biota are not well documented. Chlorine dioxide is technically feasible as a wastewater disinfectant, as demonstrated by short term operation at a full scale wastewater plant, but operational costs are high because of the price of the feed chemical. Capital costs are comparable to chlorine, with only a slight modification of generation and feed equipment necessary. Total costs tend to be 2-5 times as high per m^3 as chlorine.

- **Peracetic acid (PAA)** exists as an equilibrium mixture with hydrogen peroxide, acetic acid and water and is produced in the UK, solely by Interox, under the trade name Oxymaster (12% w/w PAA). Application of PAA is simple and direct and it is suitable for disinfection of all sewage types. Whilst it has been shown to be an efficient bactericide at concentrations of 15-20 mgl^{-1} PAA and 2 min contact time; it is less effective as a virucide and sporicide, with dosages of 100 mgl^{-1} and contact times of 30 min required for viral inactivation.

  The constituents of Oxymaster are known to cause toxic and mutagenic effects, but its rapid reaction and dissipation means that significant residuals are unlikely to occur. The highly oxidative nature of PAA makes it capable of reacting with organic compounds in wastewater; there is concern over the possible formation of epoxides and (through free chlorine formation by peroxide radicals) chlorinated organic compounds. Concentrations might be expected to be low but there are currently inadequate data to evaluate the significance of this aspect. By-products were not detected in seawater during disinfection trials with PAA. Although capital costs for PAA are low, the high feed chemical costs means that operating costs may be up to 6 times those of chlorine per m^3 of sewage treated.

- **Bromine chloride** is an interhalogen compound formed from an equilibrium mixture of bromine and chlorine. It is hazardous at low concentrations; although the reliability of storage and dispensing methods have improved, this has been a major constraint in its widespread application. Hydrolysis products of bromine chloride react with nitrogenous compounds to form bromamines (analogous to chloramine formation by chlorine). The inorganic bromamines are more effective bactericides than inorganic chloramines while organic bromamines also display some disinfectant properties. Though chlorine and bromine chloride are equally effective as bactericides, bromine chloride is a more efficient virucide, particularly in the presence of organic or inorganic interfering substances.

  Bromine-chloride is less toxic to fish than chlorine because of the shorter half-life of its residuals. However, formation of brominated THMs may pose more serious problems than the chlorinated analogues. Brominated organic compounds can accumulate in fish exposed to effluents disinfected with bromine chloride. Bromine chloride requires much the same handling and dosing equipment as chlorine but due to the higher rate of reactivity of bromine chloride, smaller contact tanks may be used thus reducing capital costs. Operating costs are reportedly of the same magnitude as those for the chlorination/dechlorination process.

- **Ionising radiation** has been investigated as both a sludge and wastewater disinfectant; it is already used in over 30 countries to increase the shelf life of food. Radiation energy can be produced from an electron accelerator or a gamma-radiation source such as Co-60 or Cs-137. Energised electrons produce a much higher dose rate than Co-60 or Cs-137 sources but, unlike gamma radiation sources, have a relatively short penetration range. Although effective in the inactivation of most pathogens, the safety aspects and high costs involved are serious drawbacks. Costs arise from the handling and shielding equipment and source replenishment. Gamma-radiation tends to be cheaper than electron acceleration at small facilities due to the investment costs of a high voltage accelerator. Although there is considerable industrial experience in the US with the use of gamma-radiation sources, radiation is inherently hazardous and requires proper protection and shielding facilities.

c) Possible disinfection techniques

Embryonic techniques considered included bromine; heat; sensitized photo-oxidation; quaternary ammonium compounds; activated carbon adsorption; protein precipitants; filtration; and ultrasound. Although several have been evaluated at pilot scale for the disinfection of wastewater, technical limitations (filtration, ultrafiltration) or cost considerations (activated carbon, heat) mitigate against their use at full scale. None were considered to provide a viable technique which could be developed for application within the next 5 years, although ultrasonication could be a useful pretreatment method for ozonation and UV irradiation.

d) Comparisons of alternative disinfectants

Comparative summaries of both operational and experimental disinfection systems are given in Tables 1 and 2.

* In considering **inactivation efficiency**, it appears that the most effective disinfectants in terms of the range of doses required for bacterial and viral inactivation are chlorine dioxide followed by ozone (see Figure 1). UV and gamma-irradiation also appear effective, although data on viral inactivation in wastewaters are limited. The halogens, bromine chloride and bromine, are more effective than chlorine as virucides, though as bactericides their efficacies are comparable. PAA requires high doses to be effective as a virucide. Chlorine, both free and combined, is an efficient bactericide but its use as a virucide appears limited. The limited information available on lime treatment suggests that the Clariflow process is likely to be effective for virus inactivation.

* The potential for **residual toxicity** effects on the marine environment is dependent on the half-life of the residual. Chlorine has the greatest hazardous potential, although the use of dechlorination with sulphur dioxide can attenuate toxicity. This is particularly important in relation to discharges to small rivers (as in many cases in the US), where the capacity for dilution is much less than for marine discharges. Bromine residuals are generally shorter-lived and both bromine and bromine chloride have been shown to be less toxic than chlorine. Whilst PAA may have a toxicity equal to that of chlorine, it is unlikely to have a significant effect in practice because it is unstable and short-lived. Although demonstrably toxic, ozone appears to present few problems regarding residuals, due to its short

Figure 1 Inactivation ranges for different micro-organisms relative to E.coli for alternative disinfectants

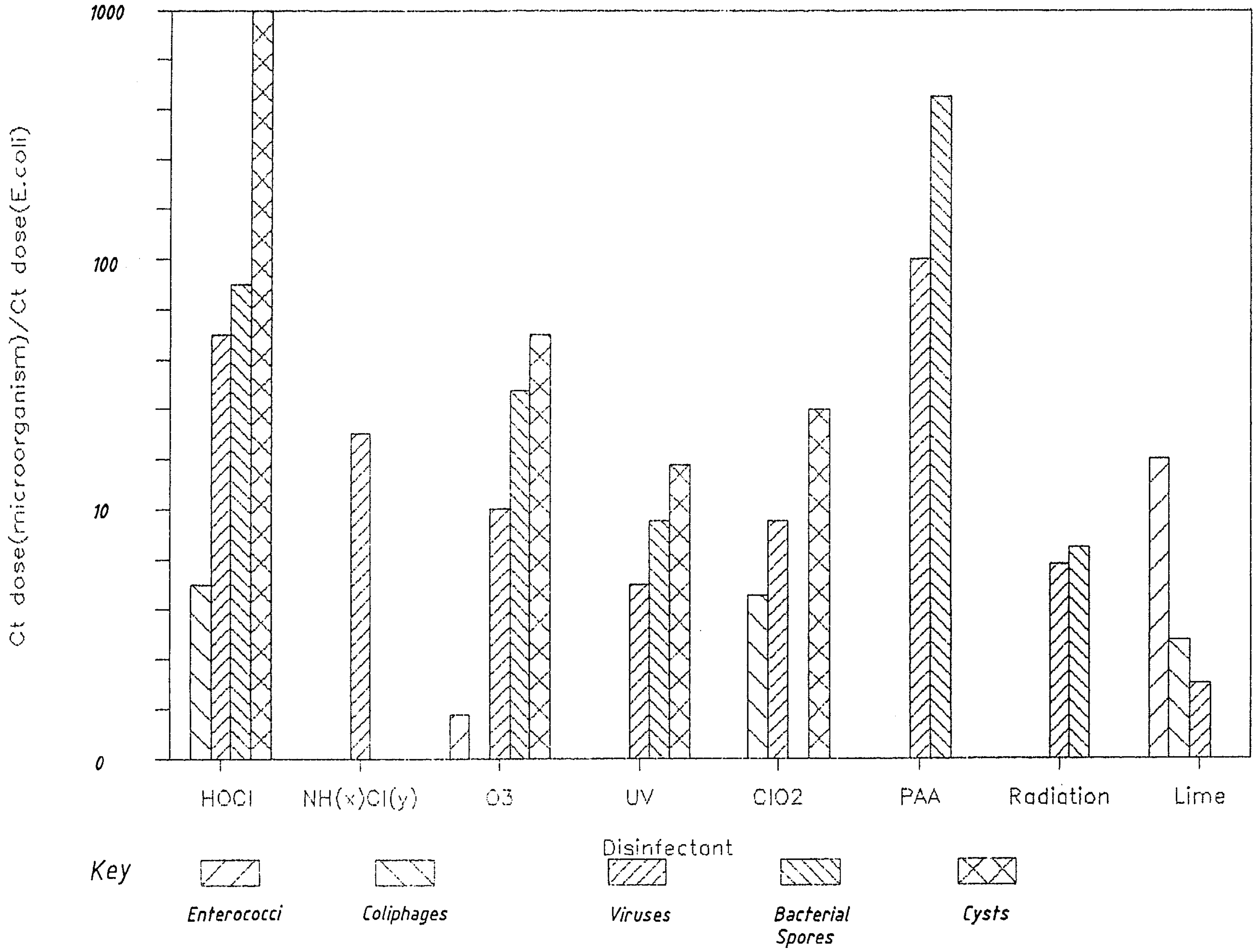


Table 1: Summary of operational wastewater disinfection techniques

	Chlorine Gas	Sodium Hypochlorite	OSEC	Ozone	UV	Clariflow
Bactericidal	good	good	good	good	good	good
Virucidal	poor	poor	poor	good	good	good?
Regrowth	yes	yes	yes	no	yes	no
Fish toxicity	toxic	toxic	toxic	none expected	non-toxic	localised
Hazardous by-products	yes	yes	yes	minimal	no	sludge
Corrosive	yes	yes	yes	yes	no	no
Community safety risks	yes	no	no	no	no	no
Operator safety risks	high	moderate	moderate	moderate	low	low
Transportation	substantial	substantial	no	no	no	sludge disposal
Relative complexity of technology	simple - moderate	simple	moderate	complex	simple - moderate	moderate - complex
Process control	well developed	well developed	developing	developing	developing	developing
Equipment reliability	good	good	fair-good	fair	fair	?
Size of plant	all sizes	all sizes	small - medium	medium - large	small - medium	small - medium
Pretreatment required	none	none	none	secondary	secondary	none
O + M sensitive	minimal	minimal	high/ moderate	high	moderate	high/ moderate
Total costs	low	low	moderate	high	moderate	high

Table 2: Summary of experimental wastewater disinfection techniques.

	Chlorine dioxide	PAA	Bromine-chloride	Irradiation
Bactericidal	good	good	good	good
Virucidal	good	poor	fair-good	good
Fish toxicity	toxic	toxic	moderate	?
Hazardous by-products	some	?	yes	?
Corrosive	yes	yes	yes	no
Community safety risk	no	no	yes	yes
Operator safety risk	high	moderate	high	high
Transportation	no	substantial	substantial	yes
Relative complexity of technology	moderate	simple	moderate	complex
Process control	no experience	developing	developing	developing
Size of plant	medium-large	all sizes	all sizes	?
Pretreatment required	none	none	none	none
O + M Sensitive	high	high	high	high
Total costs	moderate	moderate	moderate	high

half-life and rapid dissipation from water. There is little available information on UV, which cannot exhibit a direct toxic effect but may cause a physical alteration of certain compounds and hence an indirect toxic effect.

* **By-product formation** by chlorination is unequivocal and health hazards of eg. carcinogenic THMs, are widely documented. The environmental effects of wastewater chlorination have been demonstrated in trials by Welsh Water, where bioaccumulation of chlorinated organics in marine biota was observed. However, a decline following termination of disinfection may have implications for seasonal disinfection, suggesting that there may be potential for a degree of purification of the biota during non-disinfection periods.

The effects of by-products formed by alternative disinfectants are still largely unquantified. Whilst the strongly oxidative nature of ozone, PAA and chlorine dioxide may be expected to alter the components of the effluent matrix, many of the oxidation products do not appear to be harmful. By-products of concern are aldehydes, hydroperoxides and mutagenic activity of ozone; peroxides (possibly mutagenic) and small amounts of chlorinated organic compounds by PAA through generation of free chlorine; and brominated organics by bromine and bromine chloride. Generation of halogenated organics may occur with chlorine dioxide if free chlorine is present, although chlorine dioxide itself does not form THMs. There is no evidence for mutagenic activity of chlorine dioxide. Gamma-irradiation would be anticipated to cause mutagenic activity, but there is insufficient operational experience to provide evidence for this in practice.

Due to the lack of long-term operation of any of the disinfection processes other than chlorine, evaluation of their hazardous effects remains largely unresolved. However, whilst the absence of any deleterious effects seems unlikely, it would seem that the environmental impact of disinfectants such as ozone and UV will be of a lesser magnitude than that arising from the use of chlorine compounds.

* The relative **costs** of the different processes as reported in the literature are specific to a particular plant size. For example, chlorine shows distinct economies of scale and whilst there is no technical limit on the size of a UV plant, the costs tend to become prohibitive at larger facilities because of the high operating costs. On an economic basis, chlorine, hypochlorite and UV (at small-medium plants) are the most cost effective. However this does not take into account any remedial costs for precluding adverse environmental effects, eg. by dechlorination. A dechlorination system, necessary to prevent residual chlorine toxicity, adds 30-50% to the costs of chlorine and sodium hypochlorite systems, and makes them comparable with the costs of the halogens such as bromine chloride and chlorine dioxide. Also additional benefits of a process such as colour removal with ozone or phenol destruction with chlorine dioxide, are not accounted for in a simple cost analysis. Ozone is generally reported to be some

2-8 times more costly than chlorine, sodium hypochlorite approximately equal to chlorine, and chlorine dioxide and bromine/chlorine up to two times as expensive as chlorine.

Costs obtained from UK manufacturers for a theoretical case study based on a population of 25,000 and a DWF of 4,500 m^3d^{-1} are shown in Table 3. From this it can be seen that the costs of disinfecting crude sewage, for which not all systems are appropriate, increase according to the following series;

Cl_2(gas) < Cl_2(hypo) < Cl_2(OSEC), PAA < Clariflow

As with all chemical disinfectant systems, there is greatest sensitivity of cost to dose. The costs given for chlorine are based on a low dosage of 20 mgl^{-1} typically used in pilot studies but estimates are also given for a higher dosage of 100 mgl^{-1}, as used at a full-scale UK plant. Chlorine gas and hypochlorite remain the cheapest options even at higher dose rates; whilst the cost of OSEC approaches that of PAA. OSEC is significantly cheaper than the Clariflow process, which is the most expensive option with a total cost approaching that of land-based treatment. However, the Clariflow system does have additional benefits such as removal of BOD, SS and heavy metals. There are insuffient data to evaluate the costs of ozonation of crude sewage because it is generally only used for treated effluents. Assumed costs based on the latter are intermediate between PAA and Clariflow.

For the disinfection of secondary effluents, costs increase as follows;

Cl_2(gas) < Cl_2(hypo) < Cl_2(OSEC) < UV, PAA < O_3

There is a smaller range between alternatives for treated effluents; UV appears attractive particularly if compared with chlorination plus dechlorination, and is of a similar cost to PAA. Ozone remains one of the most expensive options. The comparative magnitude of process costs obtained in the case study is similar to that reported for operational plants; absolute costs vary with plant size and effluent quality.

e) Water Authority attitudes to disinfection

A summary of disinfection trials carried out by Water Authorities is given in Table 4. The general concensus among Water Authorities would appear to be to opt for long sea outfalls wherever possible. Even with adequate screening and disinfection, the public acceptability of swimming in sewage polluted waters is questionable. Although there is a great deal of interest in the potential for disinfection, there is a general reluctance for its adoption on a long-term basis because of the lack of proven efficacy and the high operating costs. The awareness of environmental impact observed by water authorities, both in-house and increasingly amongst consumers, also tends to mitigate against disinfection. It is however being seriously considered, as for example by South West Water, as a short term measure while outfalls

Table 3: Summary of estimated total treatment costs (1988) for hypothetical UK application of disinfection processes

Disinfection process	Total cost (pm^{-3})[1]			
	Screened raw sewage		Biologically treated sewage	
	6 month operation	12 month operation	6 month operation	12 month operation
gaseous chlorine[2]	2.0-5.5[3]	1.6-5.1	(1.4)[4]	(1.1)
hypochlorite solution[2]	2.1-7.0	1.7-6.6	(1.5)	(1.2)
on-site electrolytic chlorination	3.8-15.2	2.4-9.6	(2.6)	(1.6)
ozone	no data assume=20	no data assume=13	12.8	7.3
ultraviolet irradiation	not appropriate	not appropriate	4.9	3.5
peracetic acid	11.6	10.9	(4.0)	(3.5)
Clariflow[5]	26.9	18.5	not appropriate	not appropriate

[1] based on 1988 prices - includes amortised capital costs and full operation and maintenance

[2] if dechlorination using sulphur dioxide was adopted, costs could increase by approximately one third

[3] range of costs based on low (20 mgl^{-1}) and high (100 mgl^{-1}) dosages.

[4] figures in parentheses are approximate estimates for low dosages extrapolated from raw sewage applications

[5] costs influenced significantly by local sludge disposal situation

Table 4: Summary of Water Authority pilot wastewater disinfection trials

Water Authority	Chlorine (ICI)	Sodium Hypochlorite (ICI)	Ozone (Ozotech)	UV (Hanovia)	Clariflow (Blue Circle)	PAA (Interox)
Anglian			Clacton (1986)			Clacton and Southend (1987)
North West		Blackpool (1983)				
Southern+		Barton-on-Sea (1984)			Sandown* (1984-date)	
South West		St.Agnes (1987)		Par and Ladock (1987)		Plymouth (1987)
Welsh	Pwll (1978)	Bishopston (1979)				Bishopston (1979)
Wessex	Weston-S-Mare* (1976-1983)	Weston-S-Mare* (1983-date)				Weston-S-Mare (1987)

* Full scale operation

\+ A full scale OSEC plant at Portsmouth was abandoned.

are constructed.

f) Conclusions

There are several processes available which can disinfect sewage to achieve coliform levels permitting discharge through comparatively short outfalls. Estimates of UK costs show prices ranging from approximately 1.6 pm^{-3} to 19 pm^{-3} for year-round disinfection or 2.0 pm^{-3} to 27 pm^{-3} for six monthly operation. These costs would reduce slightly for very large outfall schemes, and in some cases such as Clariflow, are associated with additional benefits such as increased BOD, SS and heavy metal removal. In this respect (although not included in the present remit), it would be of interest to compare the costs of disinfection options with those for a long sea outfall. The figures presented should also be viewed in the context of the costs levied by Water Authorities for full biological treatment for subsequent discharge to an inland watercourse, typically approaching 25 pm^{-3}. In relation to this, those processes at the lower end of the cost range indicated may be attractive if they can be shown to be environmentally acceptable.

A major drawback with disinfectants is the formation of hazardous by-products. It is difficult to interpret existing information in the context of the marine environment rather than in relation to human consumption, since much of the toxicological data for chlorinated by-products relates to exposure via drinking water. The processes with the least by-products are either very costly or not presently effective for raw sewage. The only option without associated by-products is a long sea outfall. Until further evidence proves otherwise, it is considered that disinfection by chemical means should only be used on a short term basis, while an outfall is being constructed. It is interesting to note the apparent recovery of marine organisms from the effects of chlorinated discharge in the Welsh Water study; this suggests that seasonal disinfection may be less environmentally detrimental than year-round treatment. Nevertheless, the possible establishment of reservoirs of pathogens in sediments during the winter months would have to be reviewed at individual locations.

Where standards are imposed rigorously and beaches have to remain open for five years or so until an outfall scheme (or land-based treatment) comes on-stream, a choice of disinfectant may well have to be made. If economic considerations prevail, chlorine compounds (specifically hypochlorite) are attractive. Seasonal application and dechlorination to preclude residual toxicity could be used to reduce environmental impact. However, experience at Weston-Super-Mare, where dosages at the upper end of the chlorine range in Table 3 are applied and compliance is still not always achieved, has to be borne in mind. Although about three times more expensive than gaseous chlorine, the lower degree of by-product formation associated with chlorine dioxide suggests that it merits further investigation as a wastewater disinfectant.

If economic aspects are not overriding and minimal environmmental impact is considered important, the Clariflow process could have application. However, construction time, land acquisition, sludge disposal and an overall cost approaching that of land-based treatment would have to be considered. Ozone is a potentially attractive option in economic comparison to Clariflow, but its efficacy on crude sewage is not well documented. The intermediate option in terms of both cost and likely impact is PAA, however it is not possible to assess the latter factor adequately on the basis of current data.

An examination of embryonic technologies for sewage disinfection identified no systems which showed sufficient development potential for use within the next five years. Aspects identified for further research include the following:

* a detailed review of existing installations and operational experience in the US, particularly with regard to environmental effects;

* more comprehensive studies on the efficacy of alternative disinfectants for viral inactivation;

* an evaluation of effects of the use of viral indicators and of the phenomenon of viable, non-culturable cells on the apparent efficiency of disinfectants;

* field trials to assess the degree and significance of by-product formation by disinfectants, particularly chlorine, chlorine dioxide and PAA;

* a practical investigation of the applicability of chlorine dioxide for UK marine discharges.

1 INTRODUCTION

Marine discharge of wastewater relies on the dispersion, dilution and decay of sewage solids and associated microorganisms for acceptable disposal. Properly designed and located marine outfalls can achieve this at a cost of approximately 20% of that of equivalent land based treatment sytems. However, many of the 1000 or so outfalls around the UK coastline are inadequate, discharging at or near the the low water mark or providing insufficient dilution and dispersal to prevent contamination of adjacent beaches and inshore areas.

Sewage pollution is of concern on a number of grounds including:

a) microbiological contamination of bathing water and/or shellfish may cause illness in swimmers and/or consumers;

b) formation of visible slicks and deposition of sewage solids in public amenity areas causes aesthetic affront;

c) discharge of organic and metallic contaminants may result in long term environmental deterioration.

Potential health risks from swimming in sewage polluted water have been assessed in a number of epidemiological studies. An early UK study of the incidence of poliomyelitis and enteric fever by the PHLS concluded that the risk was negligible. However, subsequent investigations have shown that swimmers are more likely to report health problems than non-swimmers at the same locations, and that symptoms can be related to water quality (Cabelli *et al* 1982, 1983; Dufour, 1982; Foulin, 1983; Fattal *et al*, 1986). A recent UK study showed a significant association between the reporting of illness and swimming at a particular resort with high levels of faecal indicator bacteria, although no causal link was inferred (Brown and Campbell, 1987).

Although the methodology of epidemiological studies, in which risk assessment is related to water quality, is somewhat controversial (Lacey and Pike, 1988) it would appear that the original conclusion of the PHLS may now require re-evaluation and current attitudes of the medical authorities in the UK reflect this.

In order to minimise the public health risk, water quality standards for coastal waters have been set. In the UK, aspects of marine discharge are controlled by standards specified in various EEC Directives. Those relating to microbiological quality are summarised in Table 1.1. The standards set are based largely on faecal indicators, since testing for specific organisms is only required when 'an inspection in the bathing area shows that the organism may be present or that the quality of the water has deteriorated'.

There has been considerable discussion over the validity of using faecal indicators, particularly in relation to the risk of viral disease. Viruses are thought to be responsible for a large proportion of swimmer-associated gastro-intestinal disease (Cabelli *et al*, 1980) and have been implicated in outbreaks resulting from consumption of contaminated shellfish (Vaughan and Landry, 1984). However, they are frequently detected in marine waters in the absence of total and faecal coliforms (Tyler, 1985).

The use of alternative indicators such as faecal enterococci has been considered, as these have been found to give closer correlation with outbreaks of gastro-enteritis in swimmers (WPCF Disinfection Comm., 1987). This may be related to the longer survival time of enterococci reflecting that of viruses, which are generally more resistant to environmental stress than bacteria. Other proposed indicators include acid-fast bacilli, coliphages and cyanophages. An alternative to seeking an appropriate indicator is to direct efforts towards refining viral enumeration techniques, which are currently complex, time-consuming and costly. This would permit the direct determination of viruses during routine

Table 1.1 Microbiological standards for saltwater arising from EEC Directives.

		Protection of bathers		Protection of shellfish
		G(1)	I(2)	G(3)
Faecal coliforms	MPN 100ml^{-1}	100	2000	300
Total coliforms	MPN 100ml^{-1}	500	10000	-
Faecal streptococci	MPN 100ml^{-1}	100	-	-
Salmonella	MPN 1l^{-1}	-	0	-
Enteroviruses	MPN 10l^{-1}	-	0	-

(1) Guide value, to be observed if possible. Standard defined as an 80 percentile for total and faecal coliforms and a 90 percentile for faecal streptococci.

(2) Mandatory value. Standard defined as a 95 percentile.

(3) Guide value applying only in waters designated in the Shellfish Directive (79/923/EEC). Value applies as a 75 percentile to shellfish flesh and intervalvular fluid, but pending a further directive this value is also to be observed in waters in which live shellfish directly edible by man.

monitoring of bathing water quality. Development by researchers at the University of Arizona of a gene probe to detect viruses in water at levels of 10 per 1000 litres, within one day, appear promising.

Notwithstanding analytical considerations, compliance with the EEC Directive for bathing water quality (76/160/EC) is required at 397 coastal locations which have been designated by DoE as bathing beaches. The distribution of these according to water authority region and the rate of compliance is shown in Table 1.2. Specific water quality standards must also be observed in designated shellfish waters, according to Directive 79/923/EC. Action by the water authorities to achieve the requisite standards is largely taking the form of provision of long sea outfalls. Advanced modelling techniques using physical, hydrological and microbiological data now used in the design and location of outfalls ensures that there is sufficient dilution and exposure of discharges to ultraviolet (UV) radiation to achieve the required bacteriological standards at adjacent beaches.

However, a number of factors mitigate against the use of long sea outfalls, including:

a) high capital cost

b) long lead times for construction

c) unsuitability for certain sites due to the nature of the coastline.

There is also concern that although achieving coliform standards, long sea outfalls may permit accumulation of bacterial and viral pathogens in sediment reservoirs near the discharge point. Viral survival is enhanced by adsorption to particulates and has been reported as 17 months at mid Atlantic sludge dumping sites (Goyal *et al*, 1984). Sediment resuspension and transport could therefore lead to contamination of nearby beaches or

Table 1.2 Number of designated bathing beaches in UK water authority regions and rate of compliance with EEC bathing water quality standards.

Region	Number of designated beaches	Number compliant in 1987
Anglian	28	18
Northumbrian	19	10
North West	30	9
Southern	65	38
South West	109	96
Thames	2	0
Welsh	47	28
Wessex	38	32
Yorkshire	22	20
Northern Ireland	14	11
Scotland	23	19
TOTAL	397	281

shellfisheries.

An alternative to the use of long outfalls is to disinfect sewage prior to discharge through existing short outfalls. Disinfection has the following advantages:

a) low capital cost

b) rapid installation

c) readily extended capacity.

Rapid installation is of significance in the light of currrent pressure for compliance with EEC standards, while the capacity for expansion means that disinfection can be used flexibly to cope with large summer population increases at resorts. The disadvantages of disinfection are the high operating cost, the potential environmental impact of both disinfectants and their by-products, and uncertainties regarding inactivation efficiency for certain groups of microorganisms.

Chlorination has been the most widely used disinfection system due to its ease of application, flexibility and low cost. It is well established as a potable water disinfectant in the UK and as a wastewater disinfectant in the US. However, increased awareness of the possible environmental impact of chlorination has led to the development of alternative disinfection systems, with ozone and UV irradiation now both widely used as wastewater disinfectants overseas, largely for treated effluents. In addition, a patented lime treatment process for the disinfection of raw, screened sewage has been operational in the UK since 1985.

Other disinfectants which are either currently in use as potable water disinfectants (chlorine dioxide), swimming pool disinfectants (bromine), or adapted from specific disinfectant uses (peracetic acid (PAA), bromine chloride) have been considered as potential techniques for wastewater disinfection. Gamma-radiation, currently in use as a sludge disinfectant, is also under review.

The objectives of the present study were to review both current operational techniques and experimental techniques for the inactivation of bacteria, viruses and pathogens in sewage effluents, with particular reference to marine discharges. The inactivation efficiency of the various techniques was to be compared and the actual or potential capital and operating costs evaluated. In addition, promising techniques for future application and aspects of disinfection requiring further research were to be identified.

The report covers firstly the properties of individual operational or experimental disinfectants, reviewing their production and application; chemistry; mechanism of disinfection; inactivation efficiencies; factors affecting efficiency; and environmental impact. Operational and cost data from pilot and full scale trials, both reported in the literature and provided by UK Water Authorities are presented. Subsequent sections of the report comprise a cross comparison of disinfectant alternatives in terms of their inactivation efficiency, environmental impact and cost; and a brief summary of Water Authority attitudes to disinfection. Factors affecting the choice of disinfectant have been discussed and areas for future research identified. There has of necessity been some duplication of information within different sections of the report, but this has been retained to facilitate sectional reading only. Key findings and conclusions have been presented in condensed form in the executive summary.

Operational Disinfection Techniques

2 CHLORINATION

2.1 Introduction

Chlorination of sewage for disinfection purposes was first carried out in Britain in 1879 when chlorinated lime was used to treat the faeces of typhoid patients prior to discharge of the wastewater to sewer. It is now the commonest method of wastewater disinfection in the US, and its use is expected to increase. It has not gained full acceptance for sewage treatment in the UK but the need for compliance with the EEC bathing water quality standards together with mounting public pressure, has necessitated a critical appraisal of its merits.

Chlorination has been adopted as a cost effective means of achieving bacteriological standards in drinking water but its efficacy in treating crude sewage is less predictable and has certain disadvantages. The possibilities of the formation of toxic by-products, regrowth and resistance of bacteria have tempered its low cost and ease of application. However, it still remains the most practical and economical disinfectant it the present time.

2.2 Production and application

There are a number of different options available in the application of chlorine; the selection of chemical will be dependent on cost and safety considerations.

2.2.1 Liquid-gaseous chlorine

This is the principal form of chlorine used in wastewater disinfection in the US. It is produced commercially from the electrolysis of a concentrated salt solution and is then supplied in 864kg or tonne cylinders. It exists as liquid chlorine in equilibrium with gaseous chlorine. It may be withdrawn from the cylinders either as a gas or a liquid, with a maximum rate of withdrawal for gaseous chlorine of about 180 kgd^{-1}. A liquid withdrawal system is suitable for larger wastewater flows and requires an evaporator before the chlorinator. The chlorine may also be applied in solution or as a direct gas. If it is applied in solution, a chlorinator is required which produces a maximum chlorine concentration of 3500 mgl^{-1} (EPA, 1986). A gas chlorinator is composed of a pressure/vacuum regulator, a feed-rate control, a venturi-operated injection device and a flow meter (WPCF, 1986).

2.2.2 Hypochlorite

Sodium hypochlorite is a clear green-yellow liquid used extensively as a household bleach. Its application is inherently less hazardous than that of chlorine because it is used in solution. It is typically 14-15% (w/w) available chlorine and is more expensive than chlorine per unit weight of chlorine supplied. However since it eliminates the risks of transport and handling of liquified chlorine, it tends to be used at small sources in close proximity to housing where control of gas chlorination is difficult.

Entirely different equipment is needed for metering and control. The basic components of a hypochlorinator are the storage tank, a metering pump, a motor or solenoid, a feed-rate adjustment device and an injection device.

Calcium hypochlorite is a white, granular solid which is often used at small wastewater plants in the US in the form of powdered bleach. It is an unstable compound which is combustible and reacts vigorously, sometimes violently, with many common substances. The high costs of calcium hypochlorite has meant that sodium hypochlorite is usually used in preference.

2.2.3 On-site hypochlorite generation (OSEC)

The on-site manufacture of hypochlorite solution is possible by electrolysis of seawater or brine in much the same way that chlorine is manufactured but without the need for separation of the products. A direct current is passed through an electrolyte of seawater or brine. Chloride is oxidised at the anode with the simultaneous reduction of water. The chlorine gas and hydroxide ions that are produced react to form hypochlorite solution.

Anode

$$Cl^-_{(aq)} \text{-->} \tfrac{1}{2}\, Cl_{2(g)} + e^-$$

$$Cl^-_{(aq)} + 2OH^- \text{-->} OCl^- + 2e^- + H_2O$$

Cathode

$$H_2O + e^- \text{-->} OH^- + \tfrac{1}{2}\, H_{2(g)}$$

In a typical system designed for the generation of a 0.8% hypochlorite solution from brine, the electrolyser is composed of four sets of electrodes mounted vertically on a titanium chassis (Wallace & Tiernan). A salt saturator provides a saturated salt solution which, after dilution and application of a direct current from a rectifier across the anodes and cathodes, produces a hypochlorite solution. The hydrogen gas produced as a by-product is blown off and discharged outside the building.

2.2.4 Solid chloramine compounds

Due to the rapid consumption of chlorine by wastewater constituents to produce 'nuisance' residuals and the proven disinfection efficiency of inorganic chloramines, the use of preformed chloramine compounds has been investigated. Though not used commercially, several chloramine compounds have been shown to provide prolonged bactericidal activity (Kohl *et al*, 1980; Burkett *et al*, 1981). In addition they are often less hazardous to handle and less likely to produce hazardous by-products. The preparation of solid, stable N-halamine water disinfectants has been developed by Worley *et al*(1987) which are more biocidal than inorganic chloramines. Several compounds were investigated, and possible candidates for high temperature applications such as cooling towers were suggested.

2.2.5 Safety

Together with concerns about the long term physiological effects of chlorine compounds there exists the more direct hazards associated with the transport and handling of a dangerous gas.

Figures from the US show that in 1985, 90 worker injuries were reported associated with chemical disinfection equipment, which would be largely chlorine (WPCF, 1986). In addition, over the period 1971-1984, chlorine transportation led to 8 deaths and 483 injuries (EPA, 1986). Though the majority of these accidents resulted from railroad accidents, when adjusted to tons transported per km, the truck-transported cylinder accident rate was consistently higher.

Though the figures are likely to be lower in the UK, the potential for accidents will be increased if large scale wastewater chlorination is adopted. Prior to 1982 there were no regulations governing the storage of large quantities of chlorine. New HSE guidelines on chlorine storage indicate that storage of greater than 10 tonnes is subject to 'notification of installations handling hazardous substances regulations, 1982' (HS/G 40). There is still no maximum limit on the quantities stored. Tighter controls on chlorine storage will entail increased transportation and a higher risk of accidents on the road.

Chlorine gas is detectable by smell at low levels, and harmful effects of chlorine gas exposure are apparent at approximately 5ppm and higher. Temporary effects observed between 5 and 10 ppm include choking, coughing, watery eyes and lung irritation, whilst at higher dosages the effects become more long lasting and possibly fatal (WPCF, 1986). Recommended limits for occupational exposure to chlorine are 1 ppm (3 mgm^{-3}) as an 8 h time-weighted average and 3 ppm (9 mgm^{-3}) as a 10 min time-weighted average.

Though hypochlorite is inherently less hazardous because transported in solution, it is nevertheless a highly corrosive and irritant liquid. Large amounts of chlorine gas can be liberated spontaneously. Occupational exposure limits as for chlorine should be observed.

The generation of chlorination on site (OSEC) appears to offer the most acceptable solution in safety terms, eliminating storage and any hazard from the transportation of chlorine and minimising the exposure to personnel.

2.3 Chemistry

The chemistry of chlorination is well documented (White, 1986) and is essentially the same for any given application relying on the dissociation of chlorine in water to form the free chlorine residuals, hypochlorous acid, HOCl, and the hypochlorite ion, OCl^-.

$$Cl_2 + H_2O = H^+ + Cl^- + HOCl$$

$$HOCl = H^+ + OCl^-$$

Essentially there is no free chlorine at normal pH. In a clean water system at pH 7, HOCl predominates whereas at pH 8, OCl^- predominates.

Many compounds in natural and waste waters exert a chlorine demand, which is the difference between the concentration of chlorine added to the water and the total measurable residual. For example, chlorine reacts rapidly with ammonia to form inorganic chloramines:

$$NH_3 + HOCl \rightarrow NH_2Cl$$

$$NH_2Cl + HOCl \rightarrow NHCl_2$$

In drinking water treatment breakpoint chlorination is practised, at which point no further oxidation of the chloramines is possible and further additions of chlorine result in the formation of free residual chlorine ($HOCl$, OCl^-).

However in wastewater treatment, chlorination to breakpoint is not usually feasible due to the high concentrations of ammonia and other nitrogenous compounds which react immediately with hypochlorous acid. These include the ammonium ion, proteinaceous matter and constituents of urine that would require prohibitively excessive amounts of chlorine. Consequently the term residual chlorine in wastewater disinfection usually refers to the combined chlorine residuals, monochloramine and dichloramine, which have similar, if slower, microbicidal properties to free chlorine residuals.

When chlorine is discharged into wastewater the first reaction is thought to be with the inorganic wastewaster constituents, resulting in formation of inorganic chloramines. Providing that the chlorine:ammonia-nitrogen ratio is less than 1:1 on a molar basis, it is reasonable to assume that monochloramine is the dominant chloramine formed (Haas, 1988). Subsequent reactions appear to be attributable to organic constituents in the wastewater, in particular organic nitrogenous compounds. These react in an analogous manner to the corresponding inorganic compounds although usually at a lower rate. The resulting organic chloramines tend to be more stable and do not display any bactericidal properties; they are thus regarded as nuisance residuals.

Due to the uncertainty surrounding chlorine-nitrogen compound reactions in wastewater it has been suggested that the use of preformed inorganic chloramines for disinfection may be preferable. This would ensure that free chlorine is not consumed in the formation of nuisance residuals and that bactericidal activity is maintained by the slow release action of the inorganic chloramines.

It is also thought that the less reactive chlorine species would be less likely to form halogenated by-products such as the mutagenic trihalomethanes (THMs). Experiments on chlorination of wastewater, both nitrified and non-nitrified, indicate that combined residuals may suppress the formation of total organic halogens (TOX) and THMs but do not completely preclude it (Chow and Roberts, 1981). Nevertheless, there is also evidence that they can give rise to direct acting mutagens in much the same way as chlorine (Bull and McCabe, 1985).

The chemistry of hypochlorite solutions is essentially the same as chlorine with regard to residual and by-product formation. The only difference is in the pH of the aqueous solution, whereby the hypochlorite solution will have a higher pH than the corresponding chlorine solution:

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2$$

Hypochlorite solutions are buffered to pH 11; in contrast, the aqueous solution of chlorine arrives at the point of application at approximately pH 2. Though the solutions will be quickly buffered by the wastewater, there is much evidence to suggest that hypochlorite solutions will raise the pH of disinfected wastewater slightly whilst chlorine solutions will tend to lower it.

2.4 Mechanism of disinfection

2.4.1 Bacteria

Chlorine is thought to inactivate bacteria by causing damage on a wide front, involving simultaneously the cytoplasmic membrane, various enzyme systems and DNA (Fauris *et al*, 1986). Enzymes containing sulphydryl groups appear particularly vulnerable. The respiratory activities and related enzymes are situated close to the cell wall, where the sulphydryl group is prone to oxidation.

The high resistance of bacterial spores and acid-fast bacteria is thought to be mainly due to the failure of chlorine to penetrate these organisms.

2.4.2 Viruses

Inactivation of viruses can occur either through damage to the protein coat or to the nucleic acid. The mechanism of chlorine inactivation is still unresolved, possibly due to the fact that the mechanism differs for different viruses. However, the virus may retain its infectious capability after the capsid has been damaged. In terms of disinfection, damage to the nucleic acid whereby the virus is made permanently non-infectious is more desirable.

Studies which suggest that the mechanism of viral inactivation by chlorine is through capsid damage include those of Churn *et al* (1983), Taylor (1982) and Tenno *et al* (1980). Churn *et al* (1983) found that the initial action of chlorine on a DNA-containing enteric virus appeared to be through oxidation of the amino acid tyrosine on the viral capsid, which affected the adsorption properties of the virus. However, the DNA was intact and still capable of *in vitro* replication. This concurred with observations made by Taylor (1982) that chlorine can inactivate poliovirus and bacteriophage f_2 while leaving the RNA undamaged. Similarly, results from the study by Tenno *et al* (1980) indicated that hypochlorous acid attacks only the protein coat of poliovirus and does not result in any detectable change in the structure of the viral RNA.

In contrast, Olivieri *et al* (1982) found that hypochlorous acid and the hypochlorite ion rapidly inactivated the infectivity of RNA from the f_2 virus. The observed differences in activation mechanisms may be because the process by which f_2 infects its bacterium host cell is markedly different from that of human viruses such as poliovirus.

In addition, the structural organisation of the protein and nucleic acid of f_2 is different from that of animal viruses; this may have implications in the use of certain viruses as models.

Alvarez and O'Brien (1982) observed that chlorine inactivated poliovirus without causing separation of the viral components, indicating that the release of RNA from capsids was a result rather than the cause of viral inactivation by chlorine. No indication of the mechanism of inactivation was given.

2.5 Disinfection efficiency

2.5.1 Efficiency of different chlorine species

The efficiency of chlorination is primarily dependent on the chlorine species under consideration. Of the free chlorine residuals, hypochlorous acid is some 80-300 times more efficient than the hypochlorite ion, which is thought to be attributable to its low molecular weight and ionic neutrality, similar to water, which allows for rapid diffusion through the cell wall. The hypochlorite ion, being negatively charged may experience some repulsion of negatively charged microorganisms (Grabow, 1982).

It was originally thought that combined residual chlorine, comprising the inorganic chloramines, was not as effective as free chlorine. However, laboratory studies (which are frequently conducted with pure cultures of batch grown bacteria in chlorine demand-free solutions) tend to greatly underestimate the efficacy of chloramines. When sufficient contact time is allowed, chloramines prove equally as effective as free chlorine (White, 1986). However, the comparative efficiencies of the monochloramine and dichloramine fractions appears unresolved.

Table 2.1 shows the concentration x time (Ct) product of the various chlorine species in demand-free solutions and illustrates

Table 2.1: Comparative efficiencies of chlorine species in achieving 99% inactivation of various microorganisms (Olivieri, 1985).

species	*E.coli*			Poliovirus			*Entamoeba histolytica* cysts		
	pH	T°C	Ct	pH	T°C	Ct	pH	T°C	Ct
HOCL	6	5	0.04	6	5	2	7	30	20
OCl^{-1}	1	5	0.92	10.5	5	10.5	-	-	-
NH_2Cl	9	15	64	9	15	900	-	-	-
	9	25	40	9	25	320	-	-	-
$NHCl_2$	4.5	15	5.5	4.5	15	5000	-	-	-

Ct : concentration x contact time ($mgl^{-1}min$)

the comparative efficiency of different chlorine species in inactivating bacteria, viruses and protozoan cysts. The lower the Ct value, the more effective the disinfectant species at inactivation. This illustrates that at comparable pH and temperature, hypochlorous acid is a more effective bactericide and virucide than the hypochlorite ion. Much higher concentrations or longer contact times are required for chloramines to achieve comparable disinfection. The data in Table 2.1 suggest that monochloramine (NH_2Cl) is a more effective virucide than dichloramine, but a less effective bactericide.

2.5.2 Efficiency for different target organisms

In addition to chlorine species, the efficiency of chlorination also varies widely with the type of microorganism. In general, bacteria are more susceptible to chlorine than viruses, which in turn are more susceptible than protozoan cysts. The comparative Ct values for *E.coli*, poliovirus and *Entamoeba histolytica* cysts are 0.04, 1.0 and 20 mgl^{-1}min respectively.

This order of resistance has been confirmed by many other studies (Ludovici *et al*, 1975; Whitby *et al*, 1984; Hoff, 1986). Kawamura *et al* (1986), for instance, found that viruses were 10 times more resistant than *E.coli* to free chlorine. A comparison of Ct values for different disinfectants for a 99% inactivation of various microorganisms has also been made by Hoff (1986). These data again demonstrate the enhanced efficacy of free chlorine species over monochloramine, and the increased resistance of viruses and cysts. Viruses are up to 70 times more resistant that *E.coli* whilst *Giardia lamblia* cysts and *G. muris* cysts are more resistant by 2-4 orders of magnitude.

At the doses and contact times practised in conventional wastewater disinfection, typically 10-25 mgl^{-1} and 10-30 min contact time, it is therefore likely that inactivation of viruses will be much less complete than that of indicator bacteria. This has been illustrated by experiments on secondary effluent

(Fressonnet-Chambarlhac *et al*, 1983a) where a 4 log reduction of faecal coliforms, but only a 1.2 log reduction of viruses was achieved (Table 2.2). The dose necessary to obtain an equivalent faecal coliform abatement was 4-20 times higher for enteroviruses and 4.5-10 times higher for coliphages.

The absence of faecal indicator bacteria in freshly chlorinated sewage cannot therefore be taken to imply that viruses and bacterial spores are absent, since the latter are more resistant to chlorination. Typical chlorine residual levels necessary to achieve 4-5 log reductions of viruses in sewage and sewage effluents are of the order of $25mgl^{-1}$, as opposed to a conventional residual of $< 1mgl^{-1}$.

Different viruses and strains also show varying orders of resistance to chlorine, although studies to establish the order of resistance remain inconclusive, possibly due to different experimental conditions and enumeration techniques used. Table 2.3 shows the order of resistance of different viruses reported in various studies. Resistance appears to follow the series:

coxsackie B5 > poliovirus I > coxsackie A9

The magnitude of difference in resistance between species and strains of virus, however, is insignificant in relation to the difference in resistance between the major groups of microorganisms.

2.5.3 Regrowth of microorganisms

Several reports show that populations of coliforms can recover and increase after chlorination (White, 1986). Regrowth appears to be governed by such factors as the degree of dilution received by the sewage after marine discharge; water turbulence; level of nutrients; and water temperature (Irving, 1980). Regrowth appears to be more likely the greater the dilution of the effluent on discharge. It has also been reported that the pathogens

Table 2.2: Log reduction of faecal coliforms, enteroviruses and coliphages after chlorination (Fressonnet-Chambarlhac *et al* 1983a).

Chlorine dose (mgl^{-1})	Log abatement of: faecal coliforms	enterovirus	coliphage
4.3-5.9	2.3-4.3	0.34-1.17	1.93-3.03

Table 2.3: Order of resistance of different viruses to chlorine

Resistance	White (1986)	Payment *et al* (1985)	Harakeh (1987)
greatest	Polio II	Coxsackie B5	Coxsackie B5
	Coxsackie B5	Polio I	Polio I
	Polio III	Polio II	Polio II
	Polio I	Polio III	Coxsackie A9
least	Coxsackie A9		

Salmonella and *Shigella* can exhibit regrowth (White, 1986).

The possibility of microorganisms developing a resistance to chlorine comparable to that of drug resistant bacteria in medicine has been investigated by a number of researchers. Chlorination has been found to increase substantially the proportion of antibiotic-resistant, potentially pathogenic microorganisms with the effect most marked following regrowth (Murray *et al*, 1984). Bates *et al* (1977) observed a genetically stable increase in resistance of Poliovirus I, to chlorine, induced by repeated exposure to sublethal concentrations of chlorine. A threefold increase in Ct values was observed after 10 exposure cycles, although some viruses were subsequently less resistant. However, the mechanism for chlorine resistance is unclear and its occurrence is not substantiated by evidence from pilot and full scale studies.

2.6 Factors affecting efficiency

Many factors govern the degree of disinfection attainable with a given dose of chlorine; the most important are the wastewater characteristics, contact time and mixing efficiency.

2.6.1 Wastewater characteristics

The most significant wastewater characteristics are pH and the presence of interfering substances.

The distribution of chlorine species is highly pH dependent, thus efficiency tends to be lower at higher pH due to the predominance of the hypochlorite ion rather than hypochlorous acid. The major interfering substances are nitrogenous compounds, which exert the greatest chlorine demand. The high concentrations of ammonia-nitrogen in raw sewage and sewage effluents means that there is no free residual as chlorine is in the form of chloramines. However, treated secondary effluents are more susceptible to chlorination because of the relatively lower concentrations of ammonia and associated chlorine demand.

The presence of organic matter can substantially reduce disinfection efficiency through the formation of stable organic chloramines which have no bactericidal properties. Other interfering substances include bromide, which reacts to form brominated analogues and possibly bromine. The presence of bromide is thought to increase the concentrations of THMs formed and introduces a series of brominated THMs (Cooper *et al*, 1985; Haag, 1980). These reactions are of significance with respect to marine descarge because of the high concentrations of bromide in seawater. Much less is known about brominated organics than their chlorinated analogues and it is possible they may pose more serious health and ecological effects.

Chlorine also participates in redox reactions with sulphur compounds (hydrogen sulphide, sulphur dioxide, soluble sulphite salts); nitrite (NO_2^-) and ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions. The end-product of these reactions is the reduced form of chlorine, the chloride ion (Cl^-).

2.6.2 Contact time

Contact time is particularly important in wastewater disinfection because the residual chloramines which are formed require a greater contact time than free chlorine to achieve inactivation. A contact time of 30-60 min is commonly employed.

2.6.3 Mixing efficiency

Rapid and efficient mixing at the point of application is necessary to aid efficiency of disinfection and to prevent localised breakpoint chlorination. The more reactive and bactericidal portions of the chlorine residuals are thought to be formed in turbulent conditions, giving enhanced disinfection capability, and regrowth is less likely to occur.

The effect of improvements in chlorination design with rapid initial mixing, automatic direct residual control of chlorine dose and plug flow contact tanks was demonstrated in a model pilot facility by the US EPA (Venosa, 1983), in which a similar disinfection efficiency could be achieved as in existing treatment facilities, but with an overall application of 50% less chlorine.

2.7 Toxicity and by-product formation

2.7.1 Residual toxicity

Chlorine residuals of low concentration, both free and combined, are toxic to most fish and other aquatic life, reportedly at concentrations as low as 0.002 mgl^{-1}. The occurence of major fish kill epidodes in the US due to high chlorine residuals in freshwater systems was the first indication of the deleterious effects of chlorination. A re-evaluation of wastewater chlorination practices was prompted by a major fish kill episode in the James River estuary, Virginia, US in 1973. The use of the orthotoluidine method of measuring and controlling residual chlorine levels had led to a massive underestimation of actual levels, which were as high as 2.2 mgl^{-1} in the vicinity of outfalls. The high residual level was the probable cause of death of some 5-10 million fish of all species (Bellanca and Bailey, 1977).

The toxicity of chlorine to marine organisms was comprehensively reviewed by Irving and Solbe (1980), who documented lethal concentration doses for chlorine residuals and chlorinated compounds. Table 2.4 shows the lethal concentration values for chlorine residuals to aquatic organisms. Fish are more sensitive than invertebrates and susceptibility depends on the species and the stage of growth. Signs of stress include gasping at the water surface, rapid gill movements, loss of equilibrium and erratic swimming movements, loss of slime coat, haemorrhaging at the gills and base of fins, and passive floating prior to death (Ward, 1980). The US EPA have proposed that to avoid toxicity to aquatic

Table 2.4: Lethal concentration (LC_{50}) values for a range of aquatic organisms

Species	Test	Chlorine residual	Residual concentration (mgl^{-1})	Reference
fish	94 LC_{50}	total	0.08-0.26	Arthur *et al*
invertebvrates	94 LC_{50}	total	0.21->0.81	(1975)
rainbow trout yearlings	$7LC_{50}$	total	0.178-1.51	Whitby *et al* (1984)
rainbow trout	$96LC_{50}$	-	0.023	White (1986)
fathead minnows	$96LC_{50}$	-	<0.1	(Michigan, 1971)
female blue crabs	$96LC_{50}$	chlorine induced oxidants	0.86	Laird and Roberts (1980)
male blue crabs	$96LC_{50}$		0.84	

organisms, residual chlorine concentrations in saltwater should not exceed a maximum of 13 ugl^{-1} with an average of 7.4 ugl^{-1} (WPCF, 1986).

The relative toxicity of the combined residuals monochloramine and dichloramine was discussed by Thomas *et al* (1980). In studies in which rainbow trout, *Salmo gairdnerii*, were dosed with monochloramine at pH 8.2 and dichloramine at pH 6.5 (to assure stability), LC_{50} values for monochloramine were found to be 2.2-2.6 times greater than those of dichloramine, indicating the higher toxicity of the more substituted chloramine. The pH appeared to have little or no effect on the toxicity of monochloramine though there appeared to be some degree of recovery between doses of monochloramine which was not observed with dichloramine.

High chlorine residual levels also evoke an avoidance reaction in fish which gas been demonstrated in the laboratory and the field (Seegert and Brooks, 1980; Bogardus *et al*, 1978). Chlorine plume surveys conducted by Seegert (1979) compared fish distribution with total residual chlorine (TRC) in freshwater. Fish were absent where TRC concentrations were >0.11 mgl^{-1} and were generally only observed when TRC concentrations were <0.05 mgl^{-1}. Active avoidance was also observed in large schools of fish that would enter the plume only to return rapidly to their original position. Avoidance by striped bass was also observed by Middaugh *et al* (1977) at monochloramine levels of 0.3-0.8 mgl^{-1}.

Another aspect of concern regarding chlorine is the potential for formation of chemical barriers to migrating fish, particularly if discharge is to or near an estuary. On entering an estuary salmonids are already stressed due to the profound physical and chemical changes in their environment. The addition of toxic compounds, whether as a chlorine residual or by-product may cause exceedance of the stress tolerance threshold and stimulate an avoidance response. The discharge of chlorinated municipal effluent may also reduce the community complexity of macroinvertebrate communities (Osborne and Davies, 1987).

2.7.2 By-product formation

It is generally accepted that wastewater chlorination leads to significant increases in organic halogens (Glaze and Henderson, 1975; Murphy *et al*, 1975; Chow and Roberts, 1981; Jolley *et al*, 1982; Koczwara *et al*, 1983; Bouwer, 1985; Suzuki and Nakanishi, 1987). This occurs both in the presence and absence of ammonia nitrogen, although the lower reactivity of combined chlorine residuals means that smaller quantities of total organic halogens are produced in non-nitrified effluents. It is thought that approximately 1% of the added chlorine combines with organic material in secondary effluent (Jolley, 1975).

The formation of compounds has been found to be dependent on the chlorine dose rather than the concentration of organic material present and typical by-product concentrations range from 1-10ugl^{-1}. Although only present at low concentrations, certain of the chlorinated organic by-products can represent a significant health hazard due to their powerful mutagenic properties. An example is the compound MX, which has been identified as a direct acting mutagen capable of inducing chromosome aberrations in mammalian cells at concentrations of 4 ugml^{-1} (Meier *et al*, 1985).

Identification of relatively high levels of the mutagenic THMs in drinking water was the first indication of the possible harmful consequences of chlorination. Subsequently a wide range of chlorinated compounds has been identified in both disinfected water and wastewater; the potential for by-product formation is incresed in the latter by the larger range of organic materials present, which can act as precursors (Keenan and Hegemann, 1978). The following sections indicate the major groups of concern.

a) Trihalomethanes

Chlorination of a secondary effluent at Phoenix, Arizona at a dose of 1.5 mgl^{-1} resulted in a chloroform concentration of 4.79 ugl^{-1} compared to 2.88 ugl^{-1} in the non-chlorinated effluent. It also resulted in the formation of three brominated THMs (Bouwer, 1985). Lower average concentrations in the chlorinated than the unchlorinated effluent were taken as an indication of normal concentration fluctuations in the secondary effluent rather than the effects of chlorination *per se*.

Formation of THMs has been demonstrated during disinfection of two wastewater effluents from treatment plants in California. Chlorine doses of 20mgl^{-1} and 40mgl^{-1} applied to an activated sludge effluent from the Palo Alto plant and a nitrified effluent from the Dublin San-Ramon plant led to the production of halogenated organics both in the presence and absence of NH_3-N (see Table 2.5). Greater amounts of total organic halogen (TOX) and THMs were formed in the latter case due to the greater reactivity of free residual chlorine (Chow and Roberts, 1981).

Major precursors of THMs are generally believed to be natural organic compounds such as humic and fulvic acids and breakdown products arising from biological materials. It was postulated by Rook (1977) that m-dihydroxybenzene moieties in humic acid form the major reactive group for chloroform reaction.

b) Haloacids

Comprehensive studies by WRc have identified a number of other compounds besides THMs in chlorinated water, including the haloacids di- and tri-chloroacetic acid. Haloacid derivatives were observed by Glaze and Henderson (1975) folllowing super-chlorination of municipal secondary effluent.

Trichloroacetic acid has been shown to be formed in the same molar yield as chloroform (Miller and Uden, 1983) and occurs at similar

Table 2.5: Halogenated organic byproduct formation with chlorine in nitrified and non-nitrified effluent (Chow and Roberts, 1981).

Effluent	Dose ($mg l^{-1}$)	increase over 24 h (μ-mol Cl l^{-1}) THM	TOX
Palo Alto	20	0.39	7.6
(non-nitrified)	40	0.15	7.6
Dublin	20	3.9	20.8
(nitrified)	40	4.9	26.8

concentrations, of between 1-50 $\mu g l^{-1}$, in natural waters (Fawell *et al*, 1987). Chloroform, di- and tri- chloroacetic acids and 2,2-dichlorobutanedioic acid have been shown to account for 53% of the total organic halogen (Christmann *et al*, 1983).

c) Haloacetonitriles

Dichloroacetonitrile, 1,1,1-trichloroacetonitrile, bromochloro- and dibromo-acetonitriles have all been identified in investigations on natural waters. They are formed through reactions with amino acids and are believed to be very powerful mutagens (Fawell *et al*, 1987).

d) Halogenated phenols

Phenols react rapidly with chlorine to form the chlorophenols responsible for the chlorine taste in drinking water.

The formation of 2-, 3-, and 4- chlorophenol was observed in investigations into the effects of chlorination on municipal effluents by Jolley (1975) in concentrations up to 1.7 $ug l^{-1}$. Trichlorophenol and tetrachlorophenol were also identified in work by Glaze and Henderson (1975), whilst Bouwer (1985) found trichlorophenol and pentachlorophenol in approximately double the concentrations found in non-chlorinated effluent.

Many chlorinated phenols are highly toxic to fish with an extremely high tainting potential. In a study using static bio-assays with fathead minnows to establish the toxicity of chlorinated compounds, median tolerance limits for 2,4,6-trichlorophenol were 0.1-1.0 $mg l^{-1}$ and for 4-chloro-3-methyl phenol 0.01-0.1 $mg l^{-1}$ (Manufacturing Chemists Association, 1972).

e) Organic N-chloramines

Though not all organic N-chloramines have been characterised toxicologically, a model compound N-chloropiperidine has been shown to be formed in aqueous solution and possesses direct mutagenic activity in *Salmonella typhimurium* assays. In addition, chloropicrin (trichloronitromethane) was detected in low concentrations by Thibaud *et al* (1988) in chlorinated drinking waters. It was thought to be formed from organic nitrogenous compounds and humic substances.

In addition to those compounds generated in primarily domestic effluents, industrial effluents provide a major point source of synthetic organic materials, forming a pool of organic matter available for reaction with chlorine (Rogers *et al*, 1987). For example, chlorobiphenyls and polychlorinated biphenyls can be produced in wastewater containing biphenyl, a common product from the textile manufacturing industry (Gaffney, 1977). These are highly toxic compounds which have a tendency to impair reproduction. They also have a high resistance to microbial breakdown and a strong tendency to concentrate in lipid tissue. High residue levels of PCBs have been found in especially fish eating animals in the higher trophic levels of marine communities (Reijinders, 1987) and have been identified in sediments and soft tissues of molluscs near the sewage sludge dumping grounds off the mouth of the River Clyde (Halcrow *et al*, 1974). Epidemiological studies have shown evidence of adverse human health effects resulting from the consumption of fish contaminated with PCBs (Swain, 1988). It was concluded that every effort should be made to remove organochlorine compounds from potential contact with the human food chain.

An EPA report on risk assessment of wastewater disnfection comprehensively reviewed current knowledge of the toxicity of disinfectants and their by-products to aquatic organisms (Hubly *et al*, 1985). Table 2.6 summarises reported wastewater effluent levels of chlorinated by-products and their measured effect ranges. It was concluded that for all by-products except total residual chlorine (TRC) effluent levels are below levels known to be acutely toxic. Effluent levels of TRC however are within the

Table 2.6: Effluent levels and effects ranges for selected wastewater chlorination by-products (Hubly *et al*, 1985).

By-products	Reported effluent levels (mgl^{-1})	Measured effects range* (mgl^{-1})
Total residual chlorine	1.8	0.001-10
Chloroform	0.012 - 0.020	1.0 - 300
Tetrachloroethylene	0.004	10 - 800
Trichloroethylene	0.01 - 0.04	1.0 - 80
Chlorophenols	0.0005 - 0.03	0.01 - 500
Dichlorobenzenes	0.01	1.0 - 200
5-Chlorouracil	0.004	0.01 -100

* Upper limits of ranges indicate upper limits of testing.

Table 2.7: Summary of health effects associated with chlorination by-products (Condie, 1986)

Chemical Class	By-product	Toxicological Effects
Trihalomethanes	Chloroform	Carcinogenic, hepatotoxic, renal toxic
	Dichlorobromomethane	Hepatotoxic, renal toxic
	Dibromochloromethane	Hepatotoxic, renal toxic
	Bromoform	Hepatotoxic, renal toxic
Haloacetonitrites	Chloroacetonitrile	Genotoxic, developmental
	Dichloroacetonitrile	Mutagenic, genotoxic, developmental
	Trichloroacetonitrile	Genotoxic, developmental
	Bromochloroacetonitrile	Mutagenic, genotoxic, developmental
	Dibromoacetonitrile	Genotoxic, developmental
Haloacid derivatives	Dichloroacetic acid	Metabolic derangements, neurotoxic, ocular lesions aspermatogenesis
	Trichloroacetic acid	Increased hepatic peroxisomes
Chlorophenols	2-Chlorophenol	Fetotoxic, tumor promoter
	2.4-Dichlorophenol	Fetotoxic, tumor promoter
	2.4.6-Trichlorophenol	Carcinogenic
Chlorinated ketones	1.1-Dichloropropanone	Mutagenic
	1.1.1-Trichloropropanone	Mutagenic
	1.3.3-Tetrachloropropanone	Mutagenic

concentrations known to have acute toxic effects. It was noted that these effects include only acute toxicity effects (mainly LC_{50}) and do not include long-term chronic effects in aquatic organisms and may underestimate the significance of these by-products.

The potential human health effects of the major chlorination by-products are summarised in Table 2.7. Risk assessment of disinfection by-products to date has largely been centred on drinking water, to which humans are directly exposed. However, the potential for adverse health effects from disinfected effluents is low because of the massive dilution on discharge to the sea and the reduced potential for ingestion. Concern is therefore directed more towards the effect on the marine biota in the receiving environment.

The biological half-lives of chlorinated organics in the marine environment can range from 1-150 days and there is a tendency to be taken up by oil droplets or slicks that are a feature of sewage discharge (Irving and Solbe, 1980). Shellfish appear particularly susceptible to bioaccumulation of chlorinated compounds as they are harvested from shallow waters and thrive in sewage polluted waters. Evidence for the production and bioaccumulation of chlorinated compounds following sewage disinfection is given in Section 2.10.

Although the detection of organochlorine compounds in marine organisms does not automatically imply the existence of deleterious effects, many chlorinated organics are present in fish in high levels and may be toxic both to the fish and its predators (see Section 11.3.2). The lack of knowledge surrounding the risks of chlorination, together with the possibility of synergistic effects and the potential for bioaccumulation in marine biota, necessitates further research to predict the long-term consequences of discharging chlorinated effluent to the sea.

2.8 Dechlorination

In 1987 there were over 5000 wastewater treatment plants in the US using dechlorination (WPCF, 1987), and it is common practice in Canada. It is applied to reduce chlorine residuals to below levels that are toxic to aquatic life. It may also reduce the potential for the formation of halogenated organics as the formation of chlorinated compounds in secondary effluent was shown to increase with time up to 4 hours after chlorination (Jolley, 1975). However if organic chlorine compounds are produced rapidly then dechlorination will have no significant effect.

The two most common methods used commercially in the US are sulphur dioxide or granular activated carbon (GAC) though sodium bisulphite, sodium thiosulphate and biotin may also be used.

2.8.1 Sulphur Dioxide

Commercially sulphur dioxide is supplied in cylinders and requires similar dosing equipment to chlorine. It reacts with water to form sulphurous acid, though in most wastewater effluents it will be present as a mixture of sulphite (SO_3^{2-}) and bisulphite (HSO_3^-). It reacts with chlorine rediduals, both free and combined, on an approximately equal molar basis, thus approximately 1 mgl^{-1} is required to remove 1 mgl^{-1} chlorine. It is thought that dechlorination of combined residuals is slightly slower than free chlorine whilst the reaction with organic chloramines is sufficiently slow such that small amounts avoid dechlorination.

$$SO_2 + 2H_2O + NH_2Cl \rightarrow NH_4^+ + 2H^+ + Cl^- + SO_4^{2-}$$

Sulphur dioxide reacts with free or combined chlorine residuals to form oxidised sulphur products and convert chlorine to chloride.
A potential problem is that excessive dosage of sulphur dioxide leads to a depresson in pH and disolved oxygen, necessitating costly aeration.

2.8.2 Activated Carbon

Only a small number of wastewater plants practice dechlorination using granular activated carbon (GAC) in the US (WPCF, 1987). GAC is produced by controlled combustion and oxidation of an organic material. It achieves dechlorination by the reduction of the combined residuals to chloride ion though the mechanism differs for the different chlorine species. The use of GAC may simultaneously achieve other objectives in wastewater treatment, such as the reduction of TOC or removal of trace pollutants. It can reduce mutagenicity in drinking water both by application before (removal of precursors) and after (removal of organochlorine compounds) chlorination. After 6 months use in the dechlorination of drinking water GAC could still remove mutagens but not their precursors. Application for drinking water has been estimated to be 14 months by Lykins and Koffskey (1986). However, the high organic content of wastewater would reduce the operating life considerably in wastewater application.

2.8.3 Sodium bisulphite

Sodium bisulphite , because it is in liquid form, does not require the careful safety procedures practised with sulphur dioxide. Capital costs are also significantly lower. It is currently used at wastewater chlorination plants in the US (see Section 2.11.2) and at a potable treatment plant by Yorkshire Water; replacement of the existing sulphur dioxide by sodium bisulphite led to annual costs being approximately halved. As sodium hypochlorite and OSEC replace chlorine due to increased fears over safety, the use of sodium bisulphite may be expected to increase accordingly.

The chlorination/dechlorination system is more complex and costly to operate than chlorination alone and it is estimated that the total cost is increased by approximately 30-50% (EPA, 1986).

2.9 On-site-electrolytic-chlorination (OSEC)

2.9.1 Electrolysis of seawater

The potential for using electrolytic chlorination for an integrated coastal sewage treatment process was first recognised by Professor Mendia of Naples University who in 1958 developed an on-site electrolytic chlorination (OSEC) plant using seawater near Naples.

There have been two full scale wastewater electrolytic plants operating on seawater in the UK at Portsmouth and on Guernsey; these were built in the mid sixties but were subsequently abandoned (Marson, 1967; Frampton, 1969). Both were designed to operate on domestic sewage (with facilities for sludge separation at Guernsey) with treatment capacities of up to 47 m^3h^{-1} at Portsmouth and 76 m^3h^{-1} at Guernsey. Chlorine doses of 15-20 mgl^{-1} at Portsmouth and 12-180 mgl^{-1} at Guernsey achieved significant bacterial reductions but increases in power and replacement costs in the following years led to their subsequent abandonment.

Operational difficulties were also experienced at Guernsey due to a build-up of magnesium salts on the cathode which required daily cleaning; a time consuming and possibly injurious task to the operator. The high costs of replacement cells containing a platinised titanium anode, and subsequent discontinuation of production of these were also contributory factors in their abandonment.

The electrolysis of seawater has a number of shortcomings including high electrical costs, rapid anode wear and excessive maintenance. Problems associated with turbidity may also be anticipated from facilities drawing from shallow coastal waters.

2.9.2 Electrolysis of brine

The use of brine in OSEC appears to offer a more reliable method of producing hypochlorite, particularly where the seawater is highly turbid, as is the case with Britain's shallow coastal waters. Auxiliary equipment required for brine production include a water softener and salt saturator.

An on-site hypochlorite facility at Amherst, New York was described by Doan and Haines (1978), capable of treating up to 230,000 m^3d^{-1} of wastewater. Concern over the safety of the transport and handling of chlorine gas led to the choice of hypochlorite, whilst economic comparisons showed that significant savings could be made using onsite hypochlorite generation from rock-salt, as opposed to purchased hypochlorite. The electrolytic unit utilised at Amherst incorporated an ion-selective membrane. This unit was selected due to its ability to produce an 8-15% solution (compared to most other systems which produce a solution of less than 2%) and its lower power consumption. Electrical requirements were 0.9 kWh per kg of chlorine.

Capital costs on a 1978 price basis for the rock-salt system, which included electrolytic apparatus, power rectification and brine pretreatment, were estimated at $1,400 000 (approximately £800,000)and operating costs at $183,500 y^{-1} (approximately £105,000) compared to estimated purchase of 15% NaOCl at $554,800 y^{-1} (approximately £300,000).

2.10 Pilot studies

1 St. Agnes (South West Water/ICI)

South West Water conducted trials in 1987 using sodium hypochlorite at Trevaunance Cove near St.Agnes, Cornwall. This beach failed to comply with EEC bathing water quality standards on 4 out of 12 occasions in 1986 and on 1 out of 10 in 1987. The

Trevaunance Cove outfall serves a catchment with a summer population of approximately 5000 and an estimated DWF of 1000 m^3d^{-1}.

Laboratory trials were first conducted to determine the chlorine demand of the raw sewage and disinfection efficiencies at various doses and 10 min contact time. The initial chlorine demand varied with the strength of the sewage, but results suggested that a minimum chlorine dose of 15 mgl^{-1} active chlorine (NaOCl is 14-15% (w/w) active chlorine) would achieve a 3 log reduction of coliforms.

A 6d pilot study, using alternate days for disinfection, was conducted with bacterial monitoring of sewage, seawater and the bathing waters. An average of 16 mgl^{-1} active chlorine was administered throughout the trial with approximately 18 min contact time. The results of the trials on the bacterial levels in the sewage and the seawater close to the outfall are given in Table 2.8. This shows that a 3-4 log reduction in coliforms was achieved in the sewage whilst an overall 1.5 log reduction in coliforms was achieved in the seawater adjacent to the outfall. A stream and mine adit discharging directly onto the beach were also monitored for bacterial quality. The adit water was shown to have some bactericidal effect possibly due to its dissolved metal content.

Whilst a dose of 16 mgl^{-1} chlorine as sodium hypochlorite reduced coliform levels to within EEC standards for the period of the trial, allowing for dilution and die-off between outfall and the bathing beach; no clear correlation between disinfection and bathing water quality could be established due to the short period of the trial and the influence of climatic and tidal factors. Chlorinated hydrocarbons were identified in the sewage both before and after chlorination.

A residual of 9-12 mgl^{-1} within the sewage discharge led to an

Table 2.8: Results of bacterial monitoring in sewage and seawater during South West Water trials with sodium hypochlorite (1987)

Monitoring site	Chlorine residual ($mg l^{-1}$)	Total coliforms $100ml^{-1}$		*E.coli* $100ml^{-1}$	
		influent	effluent*	influent	effluent
outfall	9-12	10^8	$3x10^4$(3.5)	$3x10^7$	$2x10^3$(4.2)
seawater close to outfall	0.1	$7x10^4$	$2x10^3$(1.5)	$18x10^3$	600(1.5)

*figure in parentheses represents log reduction increase in chloroform ($CHCl_3$) from 2.6 to 7 ugl^{-1} but there was no apparent increase in any other volatile chlorinated hydrocarbons, nor was a change in seawater chloroform levels detected. The detection of small changes in chloroform levels against a large background of other compounds in seawater is unlikely particularly over the short length of the trial. Although a maximum 0.1 mgl^{-1} residual chlorine in the seawater was observed, it was thought that higher levels of chlorine at the outfall may occur which are likely to have a localised ecological impact.

2.10.2 Bishopston and Pwll (Welsh Water)

Welsh Water conducted sewage disinfection trials over the period 1977-1979 with the aims of establishing a cost-effective means of disinfection, gaining practical operating experience and determining the environmental impact on the receiving marine biota. Pilot trials established chlorine and PAA as suitable agents for disinfection which were subsequently selected for field trials at two sites on the South Wales coast.

Following the initial decision not to apply the EEC bathing water quality standards to Welsh beaches, and reorganisation within the authority, the results of this study were never published in their entirety. However, the subsequent inclusion of 46 Welsh beaches within the scope of the Directive and increasing concern for public health, has led to a renewal of interest in the findings. Despite a number of technical difficulties experienced in the course of the trial, it is one of the few comprehensive assessments of the environmental impact of wastewater chlorination in the UK.

Small scale laboratory experiments were conducted on untreated crude sewage using:

sodium hydroxide
calcium hydroxide
sodium and calcium hypochlorite
a formalin based preparation
chlorine dioxide
PAA

Failure to achieve adequate disinfection and excess sludge production eliminated the formalin preparation and the hydroxides respectively from further study, whilst sodium rather than calcium hypochlorite was chosen for economic reasons.

Pilot scale studies were conducted on chlorine dioxide,chlorine (as sodium hypochlorite) and PAA to establish the dose necessary to achieve a 3 log reduction in E.coli in 30 min, which on dilution would achieve compliance with EEC standards. No virological determinations were made due to the expense and lack of refinement in techniques at this time. The results of these trials showed that chlorine dioxide required too high a dose to be economic.

Trials were conducted during the bathing season period from June to September, 1978 and 1979. The two sites chosen for field studies, at Pwll in the Loughor estuary and at Bishopston on the Gower peninsular, were specially selected to allow an evaluation of the effects of the discharges on the flora and fauna although this was subsequently abandoned at Bishopston. Disinfection performance was evaluated in the effluent and in the bathing waters following discharge.

a) Pwll

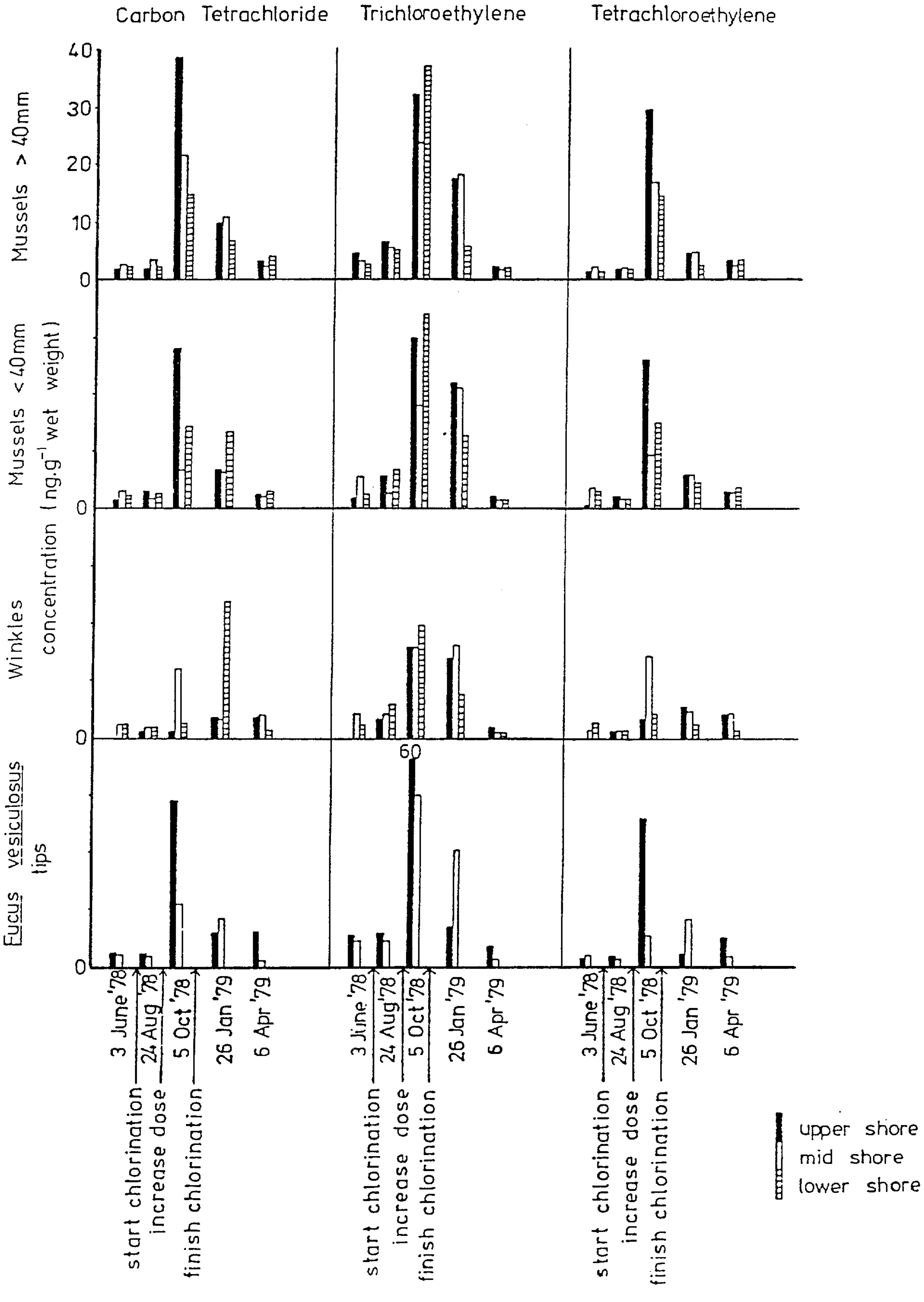
Pwll sewage treatment works on the Lougher estuary discharges primary settled sewage with a DWF of 750 m^3d^{-1} to an outfall which terminates at the mid-tide level. The presence of nearby major shellfisheries makes it a critical site for disinfection.

A gas chlorinator was installed in 1978 and an average dose of 6 mgl^{-1} chlorine and contact time of 30 min at 3DWF was achieved by diverting the effluent through a serpentine tank. The chlorine dose varied throughout the trial, with an increase in mid-September to achieve the required inactivation. Severe technical problems meant the targetted flow-proportionate dose was difficult to achieve and led to substantial overdosing, particularly at each end of the pump cycle. A mean log reduction in coliforms of 4.75 was achieved in the effluent, however bacteriological studies on the bathing waters showed no detectable difference following chlorination, probably due to contamination from a large number of undisinfected discharges.

The environmental impact of disinfection was assessed in the vicinity of the outfall and at transects along the shore. Samples of mussels (*Mytilus edulis*), winkles (*Littorina littorea*) and seaweed (*Fucus vesiculosus*) were taken from the lower, mid and upper shore on each transect and from the point of discharge, before, during and after chlorination. Throughout the trial no significant changes in the distribution and abundance of the intertidal organisms was detected at any of the transects.

The results shown in Figure 2.1 illustrate the build-up of halogenated hydrocarbons in all species irrespective of their position on the shore. Five months after the end of the trials, tissue hydrocarbon levels declined back to concentrations comparable to those prior to chlorination. The organisms on the transects further from the site of the outfall showed a trend that correlated with the dispersion patterns of the effluent. The variation in chlorine dose throughout the trial made it difficult to correlate the rate of accumulation with residual chlorine levels though a noticeable rise occurred after the dose was increased in September. There was no evidence of any acute effects on the biota throughout the short duration of the trial.

Figure 2.1 Concentrations of halogenated hydrocarbons in tissues of marine organisms collected during field trials with chlorination at Pwll, Wales (Welsh Water, 1978)



b) Bishopston

A small activated sludge works at Bishopston, on the Gower peninsular, discharges to an outfall, terminating just below the low tide mark, onto a rocky beach. Trials were conducted in 1979 with sodium hypochlorite and PAA with a concentration guide of 3 mgl^{-1} Cl_2 and 4 mgl^{-1} PAA required to achieve the necessary log 3 reduction in *E.coli*. A number of points were sampled along the shore before, during and after disinfection. Despite the short period of the study and the low numbers of *E.coli*, there appeared to be a reduction in *E.coli* numbers during chlorination with a subsequent increase after the trial ended. An ecological impact assessment was not conducted at this site due to the late start up of the chlorination facility.

The results of both the Pwll and Bishopston trials suggested that chlorination could achieve significant *E.coli* reductions in sewage effluent, though Welsh Water concluded that further work would be needed to establish the effect on bathing waters. An assessment of the efficacy of chlorine as a virucide would also be necessary to ensure disinfection was not merely a cosmetic treatment. The results of the ecological impact assessment indicated that chlorine posed a potentially serious threat to marine biota. Based on these studies, Welsh Water discounted the use of chlorine as a wastewater disinfectant, particularly in sensitive areas such as shellfisheries.

2.10.3 Barton-on-sea (Southern Water)

In 1984, Southern Water undertook trials at Barton-on-sea, Hampshire, using sodium hypochlorite. Effluent in the outfall at Barton was dosed with hypochlorite, with monitoring for coliforms and chlorine levels just after dosing and immediately prior to discharge, which allowed time for die-off in the long pipe. The results showed a reduction in total coliforms in the effluent of 2.1 logs and at the outfall of 1.2 logs.

Total coliform levels on two beaches to the east of the outfall were reduced by 1.5 logs, although reductions at two beaches to the west of the outfall were lower. Despite reasonable reductions in the outfall and at adjacent beaches, Southern Water were reluctant to proceeed with chlorination on a larger scale for several reasons, including the fact that other outfalls besides Barton were contributing to the bacterial levels. Until more information was available on the long-term environmental effects of using chlorine and the effects of non-disinfection on local beaches, it was thought that the high costs of disinfection were not justified.

2.10.4 Blackpool (North West Water)

Trials with sodium hypochlorite were conducted by North West Water in 1980. An 18 tonne hypochlorite tanker was sited adjacent to the Manchester Square Pumping Station, Blackpool, with a pump capable of delivering up to 1 m^3h^{-1}. After dosing with sodium hypochlorite, samples were taken in the land shaft approximately 100m downstream, with monitoring for residual chlorine and *E.coli*. Bacteriological monitoring was also conducted at the outfall and on the beach. Laboratory studies indicated that a 10 mgl^{-1} dose (available chlorine) could achieve a 4 log reduction in *E.coli* in 5 min, however, higher doses of approximately 20-30 mgl^{-1} were required *in situ*, due to the high chlorine demand of the effluent. Chlorine residuals of 5-10 mgl^{-1} were detected in the land shaft with occasional peaks of up to 50 mgl^{-1}. No *E.coli* were detected in the land shaft, with one exception, nor at the outfall. The beach counts were extremely variable; this was attributed to the contribution of a number of distant sources.

Concern within the authority about the probable production of THMs during chlorination and their potential effect on the marine environment led to a monitoring programme, the results of which are shown in Table 2.9. The THM levels ranged from 9 ugl^{-1} total in the untreated sewage to 147 ugl^{-1} after

Table 2.9: Results of THM monitoring in treated and untreated effluent during North West Water hypochlorite trials (ICI Tech Dept, 1980)

Sample	Chlorine residual (mgl^{-1})	THM (ugl^{-1})				
		$CHCl_3$	$CHBr_2Cl$	$CHBr_2Cl$	$CHBr_2$	TOTAL
Inlet untreated	-	23	1	<0.1	<0.1	24
Inlet treated	5	49	35	17	10	111
Inlet untreated	-	8	1	<0.1	<0.1	9
Inlet treated	10	44	49	30	24	147
Inlet untreated	-	4	11	3	1	19
Inlet treated	15	27	9	2	1	39

hypochlorination. The sample taken in the outfall boil was diluted to a maximum of 1 ugl^{-1} whilst levels 500m downstream were below detection limits (<1 ugl^{-1}).

It was concluded that whilst adequate disinfection could be achieved within the effluent, the large of number contributory sources meant that a single outfall at Manchester Square was not a viable solution. Disinfection of another major effluent source at Anchorsholme Pumping Station was considered but dismissed due to the trade effluent content and the short and damaged outfall pipe.

2.11 Full-scale operation

Unlike the developing technologies, ozone and UV, there are few data on current operational wastewater chlorination plants in the literature. The US EPA reported on several chlorination plants in their Design Manual (1986), including a gaseous chlorine and hypochlorite facility. Although no information on disinfection efficiency or costs was reported, they give an indication of current US practice in wastewater chlorination.

2.11.1 Sacramento (gaseous chlorine/dechlorination with SO_2)

A chlorination/dechlorination wastewater facility in Sacramento, California has been operational since 1982 with a design average flow of 520,000 m^3d^{-1}, averaging 490,000 m^3d^{-1} at the time of study. Pretreatment includes primary and non-nitrifying activated sludge treatment. Disinfection with chlorine gas is used to achieve permit requirements of a monthly average of 23 total coliforms 100 ml^{-1}; and a daily maximum of 500 $100ml^{-1}$. Dechlorination with sulphur dioxide is used to reduce the chlorine residual to a maximum of 0.1 mgl^{-1}.

Gaseous chlorine is supplied in 90 ton tank cars and withdrawn as a liquid into an intermediate storage tank. After evaporation, gaseous chlorine is fed to chlorinators which are controlled using a compound loop. A 13 mgl^{-1} dose is used to maintain a residual of 9 mgl^{-1} at the end of the contact system which consists of a 3000m pipe of diameter 2.6m. One chlorine analyser is situated a short distance from the inital point of application with a second at the end of the pipe.

The dechlorination system, which is calibrated twice daily, gives a sulphur dioxide dose of typically 1 mg per mg of chlorine residual plus an excess of 2 mgl^{-1} which leads to a daily dose of 5450 kgd^{-1}. Gaseous sulphur dioxide is piped under vacuum to the end of the chlorine outfall where it is mixed in ejectors and injected into the wastewater flow. Continuous pH sensors are used, although no problems with pH or depleted DO levels were experienced. Problems cited included corrosion of the chlorine analysers from the chlorine vapours emitted at the end of the contact pipe.

2.11.2 San Francisco (hypochlorite/dechlorination with sodium bisulphite)

A sodium hypochlorite/sodium bisulphite plant in San Francisco, California has been operational since 1981 (EPA, 1986). Designed for an average flow of secondary effluent of 320,00 m^3d^{-1}, it currently treats 75,600 - 756,000 m^3d^{-1}. Pretreatment includes preliminary and primary treatment followed by non-nitrifying oxygen activated sludge. Discharge requirements stipulate a 5d median of 240 total coliforms $100ml^{-1}$ and a 30d geometric mean of 200 faecal coliforms $100ml^{-1}$. This is achieved by a 12 mgl^{-1} dose of chlorine as a 14-15% sodium hypochlorite solution with 50 min contact time which maintains a residual of 6-8 mgl^{-1} (dry weather) and 3-5 mgl^{-1} (wet weather).

To comply with the requirement for a maximum instantaneous chlorine residual of 0 mgl^{-1}, sodium bisulphite as a 22% (as SO_2) solution is used to provide a 1-2 mgl^{-1} excess dose.

The main problems experienced at the plant have been in the use of the automatic chlorine control system (due to the intial disinfection of primary effluent, which fouled up the analysers) and the modification of a gaseous chlorine/sulphur dioxide system to the present one late in the design and construction phase.

2.11.3 Weston-super-Mare (Wessex Water)

Situated on the Severn estuary, Weston-super-Mare has a total summer population of >100,000. Wessex Water first introduced chlorination in 1976 when surveys of Weston beach showed failure to achieve compliance with EEC bacterial standards as each incoming tide brought sewage back onto the beach. The problem at Weston is exacerbated by the high turbidity of the water (due to the large tidal range of the Severn estuary) which requires a significantly longer exposure to sunlight to obtain a similar die-off rate in coliforms as clear seawater.

At Weston, crude sewage from the population and surrounding districts gravitate to the Black Rock pumping station where it is discharged after comminution through a short outfall (1.5m diameter) into the River Axe, ending only 22m from the Southern end of Weston Bay beach. During a large part of the tidal cycle, a significant proportion of the flow in the R.Axe is from the exposed outfall. In addition, sewage from the Brean and Uphill areas is pumped from Uphill to join the main outfall 0.5 km below Black Rock.

In 1976, emergency chlorination equipment was installed at Black Rock (at a cost of £30-40,000). Trials conducted on chlorine and chlorine dioxide had shown that a higher dose was required for the latter at a significantly higher cost. Gas chlorination equipment withdrew liquid chlorine from 1 tonne cylinders and fed it to evaporators before a chlorine solution, produced in a Venturi entrainment device, was injected into the sewage.

The need for disinfection at Uphill, together with the close proximity of housing led to the application of hypochlorite at Uphill and installation of a small hypochlorite system at Brean Merribee. In 1983, difficulties in maintaining continuous supply of chlorine gas and concerns over safety led to the substitution of sodium hypochlorite at Black Rock, despite a 10 - 20% rise in costs.

Following chlorination, average bacterial levels in the seawater close to the beach were quickly reduced to within EEC limits, except in storm conditions. Modifications to the plant in 1978-1979, increased chlorine dosing capacity to deal with storm weather flows. However, average dosages have progressively risen over the years of operation from $15mgl^{-1}$ in 1977 to the current dosing regime of $100\text{-}120mgl^{-1}$ (calculated by Wessex Water by dividing total hypochlorite used in 1987 by the total volume of sewage treated). The process at Weston is operated by monitoring the chlorine residual on the sewage at Black Rock, which is maintained at $25\text{-}30mgl^{-1}$ in May rising to $40\text{-}45mgl^{-1}$ in August. Even with such high doses there are still unexplained failures, which it was suggested may be due to clumping of microorganisms, which are subsequently broken down in the sea by wave action. In 1987, compliance at the Uphill site was 100% and at Grand Pier, marginally less than 95%. Limited viral surveys were carried out at Weston but based on information from Welsh Water it was thought that viruses were unlikely to be found (Toms *et al*, 1981).

The environmental impact of chlorination has been assessed in a number of surveys. No organochlorine compounds were detected in a sewage analysis, sensitive to $0.005ugl^{-1}$, with the exception of trace dichlorobenzene which was present in the unchlorinated sewage. This was thought to be due to the rapid formation of chloramines which react only slowly with organic matter. Fish toxicity trials, conducted using rainbow trout, showed that chlorinated effluent diluted by 200:1 in tapwater, produced no mortality over a 3d period. No dead or distressed fish were observed or reported over 3 operating years, nor was the presence of organochlorine compounds in organs of fish exposed over a 6 week period detected.

Residual chlorine levels in the bay were found to be below detection ($0.1mgl^{-1}$) with the exception of one sample taken directly over the outfall point. A slight accumulation of chloroform in limpets and seaweed from Weston Bay was observed with a maximum level of $0.025mgkg^{-1}$ in limpets immediately adjacent to the outfall, compared to <0.005 $mgkg^{-1}$ at the furthest point from the outfall. Seaweed *Ascophyllum nodosum* showed maximum and minimum concentrations of $0.015mgkg^{-1}$ and $0.006mgkg^{-1}$ respectively.

Chlorination at Weston (currently costing £150,000 per 20 week season) has never been considered a permanent solution and is looked upon as a temporary step until a properly sited long sea outfall is constructed. Implementation of a new $1000m^3$ contact tank next year, to give a longer contact time and to balance storm water flows, is hoped to improve current compliance. However, if the present arrangement does not consistently meet EEC standards then consideration will be given to construction of a long sea outfall.

2.12 Costs

2.12.1 Chlorine gas

Capital equipment for the usage of gaseous or liquid chlorine includes the following:

chlorine header to accommodate the drums
chlorine gas changeover device (automatic)
vacuum regulators
chlorinators
booster pumps
chlorine leak detector
alarms
ventilation equipment

Operating and maintenance costs mainly comprise chemical costs, though power and labour are also significant. Chlorine is delivered in 864 kg drums, at a cost of £403-430 tonne^{-1} (ICI, 1988) or 40-43 pkg^{-1}, with the price depending on delivery distance. For a chlorine dosage of 15 mgl^{-1} (gm^{-3}) this is equivalent to 0.6-0.65 pm^{-3}. Labour requirements are estimated at not more than 1 man-hr d^{-1} to carry out replenishment of chemicals, necessary adjustments, cleaning etc.

The power costs for a chlorination plant of capacity 25 kgh^{-1}, assuming one booster pump and one chlorinator are 3.3 kWh, whilst lighting would be approximately 1 kWh and heating 8kWh for 3 months of the year (Portacel Ltd).

2.12.2 Sodium hypochlorite

Capital equipment for hypochlorite includes:

Hypochlorite storage tanks
Metering pumps
electrical controls

Road tankers carrying 23 tonnes are used for delivering sodium hypochlorite, and minimum storage capacity recommended by ICI is approximately 1 weeks usage plus the contents of a road tanker. Operating and maintenance costs comprise mainly chemical costs; the costs of hypochlorite are £70-£100 tonne^{-1} (ICI, 1988) which at a dose of 15 mgl^{-1} active chlorine (107 mg NaOCl l^{-1}), leads to costs of 0.7-1.1 pm^{-3} sewage. This is up to 70% higher than for gaseous chlorine. Power costs are minimal whilst labour costs are as for chlorine.

In the South West Water trials (section 2.9.1) a dose of 16 mgl^{-1} active chlorine (equivalent to 0.09 l hypochlorite solution m^{-3}) @ £178 $1000l^{-1}$ hypochlorite led to costs of 1.59 pm^{-3} sewage. This was equivalent to daily costs for a 1000 m^3d^{-1} flow of £15.90 d^{-1}.

2.12.3 OSEC

Capital costs include the following for an OSEC brine unit:

electrolyser
water softener
heat exchanger
salt saturator
brine metering
product transfer
product storage (suitable for 1% NaOCl)
air blower (for hydrogen dilution and exhaust)
transformer/rectifier
busbars
control panel
product dosing

Power and chemical costs are the major components of operating and maintenance costs. For an electolyser of capacity 18 kgh^{-1}, electricity consumption is approximately 4-4.7 kWh kg^{-1} chlorine. Chemical salt and softener regeneration is estimated at 0.5 pm^{-3}. Maintenance is estimated at 20% higher than for gaseous chlorine. Total operating and maintenance costs are of the same order of magnitude as chlorine gas and sodium hypochlorite.

2.13 Conclusions

1. Chlorine is the most widely-used disinfectant available at the present time, with many years of proven operating experience as a wastewater disinfectant in the US. The ease of application makes it suitable for emergency disinfection or as a temporary measure.

2. It is the most economical disinfectant available with low capital costs and operating costs of under 2 pm^{-3}.

3. Chlorine is a much more effective bactericide than virucide. Compliance with EEC standards for conventional indicator organisms may still fail to meet virological standards.

4. High levels of chlorine residuals are toxic to fish and invertebrates though dechlorination techniques may be used to minimise the toxic impact. In addition many chlorinated organics have been shown to display toxic, carcinogenic and mutagenic properties, and may prove hazardous through bioaccumulation.

5. There are quantified hazards associated with the handling of chlorine gas. Revised legislation concerning restrictions on the storage of chlorine has serious implications for transportation safety, and the use of hypochlorite or OSEC should be considered as the appropriate application in densely-populated areas.

3 OZONE

3.1 Introduction

Ozone is an unstable gas, occurring naturally in the stratosphere through the reaction between atomic and molecular oxygen.

It was first discovered in 1783; the earliest investigations for municipal water treatment were performed in the late 19th century in Germany leading to full scale plants at Wiesbaden and Paderbor. Adopted by many countries including France, Spain, Austria, Russia and later UK for potable water treatment, it is also used extensively for wastewater disinfection in the US and to a lesser extent in Europe. In 1987 there were 19 operational plants in the US, of which three have only been in operation since 1985 (Robson, pers comm). In addition there are 2 small scale wastewater ozonation plants in France.

3.2 Production and application

3.2.1 Generation

Ozone can be produced by electrolysis, photochemical reaction or by the high voltage ionisation of air or oxygen. In commercial ozonation plants, oxygen in the air or pure oxygen is subject to a high voltage electrical discharge across an air gap between the high tension and earthed electrodes. The electrodes are separated by an air space of precise dimensions. A glass dielectric is used to limit the discharge and prevent direct arcing. The generators are manufactured in the form of cylindrical tubes or flat plates, a number of which are then connected in parallel.

Though oxygen is more expensive than air, higher concentrations of ozone may be obtained, typically 1.7% ozone (24-72 gm^{-3}) compared to 1% ozone (12-24 gm^{-3}) (Rakness and Hegg, 1985).

If air is used, a high level of preparation is required to provide clean, dry air to prevent damage to the generator's dielectrics and optimise ozone production. Filters are required to remove dust and oil and most importantly, dryers are necessary to provide a minimium operating dewpoint of -60°C.

In larger installations, prechilling is used to economise on dryer size; the optimum process is to compress air at low pressure, chill it and dry with a heat-generated dryer (Ozotech). Operational problems in the US and UK have involved underdesign of the air preparation systems based on an inadequate dewpoint of -40°C (Rakness pers comm). Also certain pure oxygen generation systems do not guarantee the necessary minimum dew point of oxygen and would be expected to create problems.

Heat generated by the production of ozone must be removed to prevent excessive ozone decomposition and increased energy consumption. Heat removal may be achieved using water, air, or water and freon, which is circulated around one or both of the electrodes. A schematic of the processes involved in ozone production is shown in Figure 3.1.

There are several types of ozone generators currently in use in US wastewater facilities and these are typically described by their different control mechanisms, cooling system and physical arrangement of the dielectrics:

a) horizontal tube/water cooled/low frequency (H/W/L)
b) vertical tube/water cooled/low frequency (V/W/L)
c) vertical tube/water/oil or freon cooled/high frequency (V/D/H)
d) plate dielectric/air cooled/high frequency (P/A/H).

Only the first two have given satisfactory operational experience. Frequent dielectric module failures at certain installations have lead to their abandonment or replacement at the P/A/H installations (Robson, pers comm) . Ozone generators should

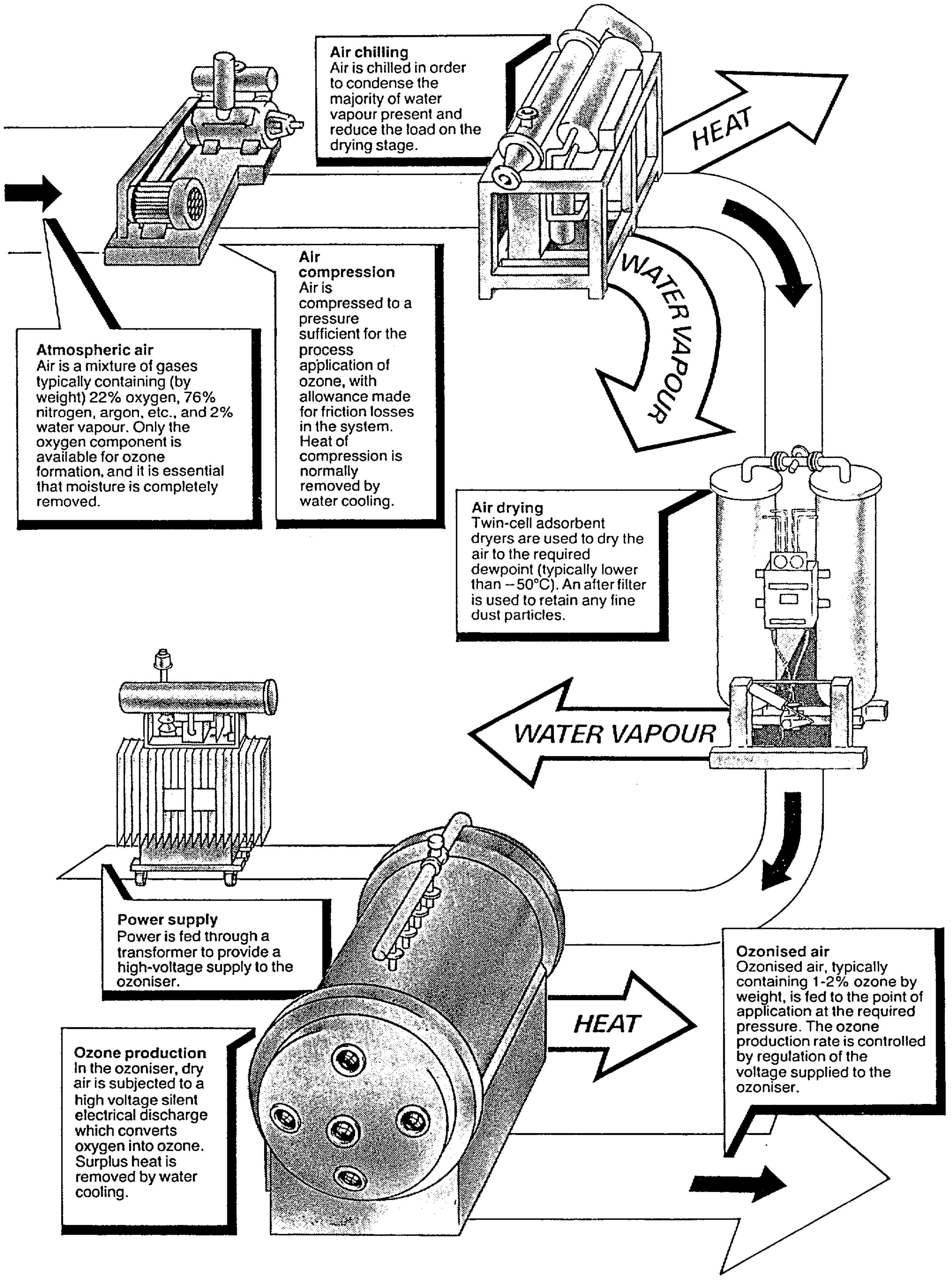


Fig 3.1 Plant for generation of ozone from air (Reproduced courtesy of Ozotech Ltd.)

Atmospheric air
Air is a mixture of gases typically containing (by weight) 22% oxygen, 76% nitrogen, argon, etc., and 2% water vapour. Only the oxygen component is available for ozone formation, and it is essential that moisture is completely removed.

Air compression
Air is compressed to a pressure sufficient for the process application of ozone, with allowance made for friction losses in the system. Heat of compression is normally removed by water cooling.

Air chilling
Air is chilled in order to condense the majority of water vapour present and reduce the load on the drying stage.

Air drying
Twin-cell adsorbent dryers are used to dry the air to the required dewpoint (typically lower than −50°C). An after filter is used to retain any fine dust particles.

Power supply
Power is fed through a transformer to provide a high-voltage supply to the ozoniser.

Ozone production
In the ozoniser, dry air is subjected to a high voltage silent electrical discharge which converts oxygen into ozone. Surplus heat is removed by water cooling.

Ozonised air
Ozonised air, typically containing 1-2% ozone by weight, is fed to the point of application at the required pressure. The ozone production rate is controlled by regulation of the voltage supplied to the ozoniser.

not be operated at 100% of full capacity for extended periods of time as experience has shown that it can stress the generator dielectrics and result in excessive maintenance requirements (Rakness pers comm - to be published).

3.2.2 Ozone dissolution

A good contactor design is crucial in reducing applied ozone levels and hence the size of the ozone generation unit. Full scale design considerations for the contact tank, are that it maximises plug flow conditions; maximises localised mixing within the plug flow system and maximises transfer efficiency (Rakness and Hegg, 1984). The contactor should be baffled to minimise short circuiting. Initial stages are designed primarily for ozone demand reactions whilst the latter stage provides a residual ozone level for disinfection. U-shaped tubes are currently being developed to allow better ozone transfer and plug flow for better control of ozone injection and use. Pilot scale results are promising and it was reported in 1986 that two commercial installations were being built (Richard, 1986).

Dissolution of ozone is difficult due to its low partial pressure in the contacting gas. Maximum mass transfer is usually achieved by forming a gas/water emulsion in the form of bubbles of an optimum 2-3 mm diameter. Ozone transfer has been shown to be inversely proportional to bubble size (Ahmad and Farooq, 1985) but very fine bubbles may be swept out of the contact basin. The performance of the contact basin is dependent on the pressure at the point of application, with an optimum 0.5 bar gauge pressure necessitating contact tanks of a 5m depth.

The most prevalent type of contactor presently in use is the bubble diffuser type (Rakness, pers.comm.); this is generally considered the most economical (Rakness and Hegg, 1985). General methods of ozone dissolution include:

a) Injection of ozone containing air through porous system (tubes or disc).

b) Injection of air, dispersion and stirring using a turbine. Energy requirements are generally about 10 times higher than for (a).

c) Injection of air through an induced vacuum injector or eductor. The head loss created is also highly energy consuming.

The diffusion techniques in (a) are normally used for wastewater plants and larger municipal drinking water plants and injection methods in (c) are used for smaller plants. Also recently developed at the University of Newcastle is the Spinning Disc Reactor (Anderson *et al*, 1985) which achieves efficient mass transfer of ozone to a thin liquid film, as it flows across a spinning disc surface.

Materials for use in ozone systems should be 304L, 316L stainless steel for piping (Rakness, pers. comm.). Threaded joints are difficult to seal therefore welded or flanged piping connections are recommended. Hypalon gaskets should be provided at flanged joints where meters, valves or other equipment are to be installed. The use of unplasticised PVC in some ozonation gas handling systems has resulted in piping failures (Robson, pers.comm.). The ozone contactor roof and walls should be lined with Hypalon coating to keep fumes from leaking into the plant (Rakness, pers. comm.).

Transferred ozone dosage may be used as a control parameter to optimise disinfection at a minimum ozone dosage. However an improved control method has been developed by Venosa and Meckes (1982) using the ozone concentration of off-gas from the contact basin. This is similar to using the chlorine residual to control chlorine dosage in that both are responsive to wastewater quality as well as changes in wastewater flow. A better correlation with coliform reduction has been achieved at a plant at Vail, Colorado, using off-gas control rather than the transferred ozone dose (Rakness *et al* 1984).

Ozone degradation to oxygen is very fast, but some ozone will always be present in the contactor off-gases which, for health and safety reasons, must be destroyed or reused. Methods include:

a) dilution with air (10 - 20 parts air:1 part ozone)
b) passage through wet granular activated carbon (normally only used at smaller potable water plants)
c) thermal destruction (300 - 400°C; heat exchangers are usually employed to maximise heat recovery)
d) thermal/catalyst - capital and operating costs are lower than with heat alone (Rakness, pers. comm.) but certain catalysts are poisoned by substances which may be present in the off-gas.

3.2.3 Safety

The generation of ozone on-site eliminates any transportation hazards and therefore the primary risks of ozone are limited to its on-site production. These include risks of human exposure to gaseous ozone; vegetation in the vicinity of the treatment plant and human contact with high electrical voltage (Hubly *et al*, 1985). Ozone is an extremely toxic gas; health effects are shown in Table 3.1. None of the symptoms associated with an exposure of less than 1.0ppm are reported to have lasting effects. Recommended occupational exposure limits are < 0.2 mgm^{-3}, as an 8h time weighted average (0.1 ppm v/v) and < 0.6 mgm^{-3} as a 10 min time weighted average (0.3 ppm v/v).

The concentrations of ozone from the generator are typically between 12-24 gm^{-3} and thus a small leak in the ozone supply piping can cause ambient ozone concentrations far in excess of those allowed (Rakness and Hegg, 1985) Though it can be detected at concentrations much lower than harmful levels, continued

Table 3.1. Health effects of ozone (WPCF, 1986).

Concentration (mgm^{-3})	Human response
0.03-0.2	Detectable odour
0.2	Irritation of nose and throat
1.0-2.0	Difficult breathing
2.0-20	Pulmonary oedema

exposure quickly tires response and adequate leak detectors must be installed. The limited data on wastewater ozonation prevent a quantitative assessment of the accident rate for workers in wastewater treatment facilities, but it is not seen as a particular cause of accidents of injuries in Europe (Hubly *et al*, 1985), nor in 70 years of large scale ozone disinfection of potable water in Canada and Mexico have there been any fatalities reported (Nebel *et al*, 1975a)

3.3 Chemistry

Ozone is a powerful oxidant with one of the highest oxidation potentials known (2.07 V in acidic solution, 1.24 V in basic solutions). It decomposes rapidly in solution, the decomposition rate increasing with alkalinity and temperature. The decomposition behaviour is complicated and all intermediates are very reactive and possess very short half-lives. Possible species in an aqueous ozone solution are the ozone molecule, the hydroxyl and hydroperoxyl radicals (OH, HO_2) and the radical ions oxide and ozonide (O^-, O_3^-) (Peleg, 1976). The hydroxyl radical, which is an even more powerful oxidant than ozone (oxidation potential = 2.8 V at 1.0 M [H^+]) is thought to play an important role at high pH.

Reaction schemes proposed for the decomposition of ozone in aqueous solution include those by Keenan and Hegemann (1978):

$O_3 + H_2O \rightarrow HO_3^+ + OH^-$
$HO_3^+ + OH^- \rightarrow 2HO_2$
$O_3 + HO_2 \rightarrow HO + 2O_2$
$HO + HO_2 \rightarrow H_2O + O_2$

and Peleg (1976):

$O_3 + H_2O \rightarrow O_2 + 2OH$
$O_3 + OH \rightarrow O_2 + HO_2$

$O_3 + HO_2 \rightarrow 2O_2 + OH$

$OH + OH \rightarrow H_2O_2$

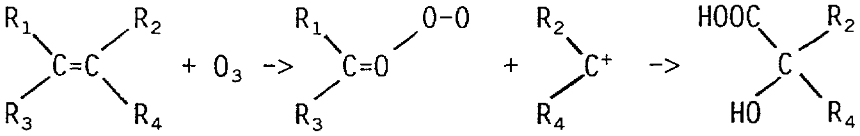
$OH + OH^- \rightarrow O^- + H_2O$

$O^- + O_2 \rightarrow O_3^-$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

In wastewater, organic compounds may preferentially react with highly reactive species such as the hydroxyl radical at the expense of disinfection. Thus it appears that the oxidation reactions of ozone are pH dependent, with faster free radical oxidation at high pH (>8.5) and slower direct oxidation at lower pH. Disinfection efficiency is therefore maximised by slower direct oxidation whereby ozone is not quickly consumed by organics and a longer lasting residual is obtained. Hard water containing bicarbonate and carbonate ions (HCO_3^-, CO_3^{2-}) can enhance slower oxidation by acting as scavengers for radical species though this is more significant in potable water disinfection (Duguet *et al*, 1987).

In direct oxidation, ozone attacks carbon double bonds, C=C, in organic compounds to give a variety of end products depending on the side chains (Nebel *et al*, 1976)



Organic peroxides exhibit some bactericidal properties, being less stable than H_2O_2, and may contribute to the total oxidant residual in an ozonated effluent.

3.4 Mechanism of inactivation

Ozone disinfection appears to occur either via a general cytoplasmic inactivation or through reaction with specific parts of the cell, depending on the microorganism involved. Since ozone often behaves as if positively charged, this may facilitate the inactivation of colloidal material by a combination of charge neutralisation and chemical oxidation.

3.4.1 Bacteria

Bacterial disinfection is thought to proceed via a general cytoplasmic inactivation of the whole cell. Ozonation of *E.coli* in studies by Ishizaki (1987) resulted in penetration of the cell membrane and inactivation of the cytoplasm. Damage of the chromosomal DNA, cell membrane and essential enzymes was also thought to be involved.

3.4.2 Viruses

Viral inactivation by ozone is thought to proceed via coagulation of the protein capsids or by oxidative disruption of the nucleic acid core.

Studies on the f_2 bacteriophage led Kim *et al* (1980) to postulate that ozone breaks the viral protein capsids into sub-units, liberating the RNA and host pili. However the RNA may retain infectivity after ozonation, which has serious implications for disinfection if the f_2 phage forms an appropriate model for enteric viruses. The RNA may be secondarily sheared by reaction of the protein modified by ozonation. Damage to the viral protein coat was also thought to be responsible for inactivation of poliovirus II and bacteriophage 174, whilst inactivation of poliovirus I was thought to occur as a result of damage to RNA (Ishizaki, 1987).

Studies on the reaction of RNA of tobacco mosaic virus with ozone reported by Rice *et al* (1981) found that preferential attack of the guanine base of the RNA may be the most important factor in the inactivation mechanism. Ozone is also known to have a particularly high affinity for sulphur-containing amino acids such as cysteine and methionine and undergoes fairly rapid reactions with most other amino acids (Evison, 1978). It has been suggested that the lower resistance of different viruses to ozone may be due to higher proportions of sulphur containing amino acids in the viral coat.

3.5 Disinfection efficiency

A characteristic of ozone disinfection is its rapidity and the low concentration required to achieve a given kill.

It is clear from the data presented in Table 3.2 that at neutral pH, ozone is more effective than either hypochlorous acid or chlorine dioxide, with lower Ct values for bacteria, viruses and cysts, although the temperature differences must be taken into account. The difference in Ct values is particularly marked for viruses and indicates the smaller differential between bacterial and viral inactivation for ozone compared to chlorine. Thus 3-14 times the concentration x time product (Ct) for *E. coli* is required to inactivate poliovirus by ozone whilst the equivalent Ct product for viral inactivation by free chlorine is 50 times that of *E.coli*.

Work conducted by Hoff (1986) on a wider range of microorganisms found Ct values for *E.coli* and poliovirus of a similar order of magnitude to those in Table 3.2. Rotavirus appeared less resistant than poliovirus and required a Ct value of 0.3-3 times that of *E.coli*. The Ct values for *G. lamblia* cysts and *G. muris* cysts were up to 25 and 100 times those of *E.coli* respectively.

Experiments on bacterial and viral inactivation in ozone demand free water also confirmed the enhanced properties of ozone over chlorine, in that a 99% kill for poliovirus I was achieved with 0.3 mgl^{-1} in 10s for ozone compared to 100s for chlorine

Table 3.2: Comparative efficiencies of ozone, chlorine and chlorine dioxide to achieve 99% inactivation of microorganisms (Olivieri, 1985)

	E.coli			Poliovirus I			*Entamoeba histolytica* cysts		
	pH	Temp (°C)	Ct	pH	Temp (°C)	Ct	pH	Temp (°C)	Ct
Ozone	6	11	0.031	7	5	0.42			
	7	12	0.002	7	20	0.005	7.8-8	19	1.5
HOCl	6	5	0.04	6	5	2.0	7	30	20
ClO_2	6.5	15	0.38	7	15	1.32			

*Ct values in $mgl^{-1}min$

(Katzenelson *et al*, 1974). A two stage inactivation curve was observed, with a short initial stage of rapid kill. A second slower reaction phase was thought to be due to clumping of the microorganisms, as shown by increased sensitivity following ultrasonication.

In a comparison of the inactivation efficiencies of ozone, chlorine and UV on seeded microorganisms in distilled water, Kawamura *et al* (1986) found that at the same disinfectant concentration, the contact time required to obtain the same inactivation efficiency was lower for ozone. The order of resistance was found to be:

spore-forming bacteria >> *Candida tropicalis* >> *Staphylococcus aureus*, *E.coli*, *Salmonella typhi*.

The reduction profiles of the spore-forming bacteria were observed to have initial shoulders, whereas the non-resistant microorganisms showed an initial sharp decline followed by a slower reduction after several seconds. Reduction rates were found to tail off at low microbial concentrations (Kawamura *et al*, 1986).

Wastewater quality has a critical effect on inactivation efficiency, due in part to increased ozone demand, but also because of encapsulation and protection of microorganisms under normal operating conditions. Table 3.3 shows that the minimum ozone dose needed as a function of effluent quality varies considerably. The contact times employed, transfer efficiencies and effluent coliform target levels all have an important bearing on the applied dose required. At all of the operational plants in the US, extensive tertiary and/or advanced wastewater treatment is practised before ozonation. Absorbed ozone dosages are in the range of 4-8 mgl^{-1} to achieve effluent targets of 200 faecal coliforms $100ml^{-1}$. Where the plant effluents contain a significant industrial component (eg Indianapolis, Springfield),

Table 3.3: Ozone dosages and contact times used in pilot and full scale studies for a range of effluent qualities

Wastewater pretreatment	COD (mgl^{-1})	O_3 dose (mgl^{-1})	O_3 residual (mgl^{-1})	Contact time(min)	Efficiency (log reduction)	Reference
Untreated urban sewage	100 - 240	2.5		19	log 1.8: E.coli log 1.6-1.9: faecal streptococci log 1: viruses	Joret et al (1982)
Oxygen activated sludge	variable	15	0.05	5	log 2: total coliforms, faecal coliforms, faecal streptococci 100%: viruses	Rice et al(1981)
Filtered secondary	39.7	15-20		15-20	}achieves <70 total coliforms }(100 ml^{-1})	Stover and Jarnis(1980)
Filtered nitrified	20.5-21.7	5-10		5-10	}	
Screening, grit/oil removal aeration, clarification	50	10	0.1-0.2	54	log 4: total and faecal coliforms	Fressonnet et al (1983a)
Screening, grit/oil removal activated sludge clariflocculation, filtration	- -	6-9	0.2-0.6	11-30	3-4 log: total coliforms	Fressonnet et al (1983a) Barraud (1983)
Coarse screen, activated sludge, nitrification, microscreening,		1.5 (transferred)		15	0.5-3 log: faecal coliforms	Rakness et al (1983)
Activated sludge, nitrification, filtration		6 (absorbed)			achieves 200 faecal coliforms (100 ml^{-1})	Rice et al(1981) (Upper Thompson)
Primary settling, oxygen activated sludge, air nitrification activated sludge, tri-media filtration		10			achieves 200 faecal coliforms (100 ml^{-1})	Rice et al(1981) (Springfield)

higher absorbed ozone dosages are required despite extensive tertiary treatment.

Ozone has been shown to be a more efficient virucide than chlorine, chlorine dioxide or peracetic acid in experiments on secondary effluent (Harakeh, 1987). A residual of 0.5 mgl^{-1} ozone achieved complete inactivation of 6 viral species in 5 min, with human rotavirus the most resistant and f_2 bacteriophage the least resistant virus tested. To achieve comparable disinfection, a residual of 11 mgl^{-1} chlorine, 5 mgl^{-1} chlorine dioxide and a dose of 140 mgl^{-1} peracetic acid were required respectively. Experiments conducted on secondary wastewaters by Pavoni *et al* (1975) found that an ozone dosage of 15 mgl^{-1}, residual 0.015 mgl^{-1} and 5 min contact time achieved complete inactivation of f_2 virus. In clean water, a complete kill was achieved in under 15s.

In one of the few studies on low quality wastewater by Joret *et al* (1982), elimination of faecal bacteria and enteric viruses in untreated domestic sewage following ozonation was investigated. It was found that a 2.2-4.1 mgl^{-1} ozone dosage with a residual of 0.06-0.35 mgl^{-1} at 19 min contact time led to abatements of 1.8 log *E.coli*, 1.6-1.9 log faecal streptococci and 1 log virus. These comparatively low reductions indicate the critical effect that wastewater quality has on efficiency.

At a full scale ozonation wastewater plant at St Michel en Grèves, France, operating on secondary effluent, a $10gm^{-3}$ ozone dose with a contact time of 54 min achieves a 4 log abatement of total and faecal coliforms. (Fressonnet-Chambarlhac *et al* 1983a). At Guëthary in France, ozonation of tertiary treated effluent at a dose of $6\text{-}9gm^{-3}$ ozone, residual level of $0.2\text{-}0.6gm^{-3}$ with a contact time of 11-30 min gave a 2-3 log reduction in total coliforms. In addition no enteroviruses were found to be present in a 20 l sample (Fressonnet-Chambarlhac *et al*, 1983b).

In general, adequate disinfection can be achieved by relatively low doses of ozone (approximately 5 mgl^{-1}) in effluent that has had secondary and/or tertiary pretreatment. For lower quality wastewaters and to guarantee viral inactivation in secondary effluents, higher doses of 10-15 mgl^{-1} may be required.

3.6 Factors affecting efficiency

All full scale wastewater plants in US and France currently operate on secondary or tertiary effluents, which indicates the importance of wastewater quality in achieving efficient disinfection. The correlation between efficiency and absorbed dose (rather than applied dose) also suggests that, for a given effluent quality the efficiency with which ozone is transferred from gas to solution is a major influential factor.

3.6.1. Transfer efficiency

For ozone to achieve disinfection it must be effectively transferred to the wastewater. The solubility of ozone in the wastewater is governed by Henry's Law and will be proportional to the partial pressure, or concentration of ozone in the carrier gas above the liquid. Though ozone is more soluble than oxygen in water, because of the low concentrations in the carrier gas (typically 1-2%) it is more difficult to obtain more than a few mgl^{-1} in solution under normal temperature and pressure. The transfer efficiency is the difference between the concentration of ozone in the carrier gas and the concentration of ozone in the gas leaving the contactor (Stover and Jarnis, 1980).

Studies have shown an excellent correlation between the transferred ozone dosage and the coliform survival rate. The transfer efficiency may be optimised by the design of the contact basin which must ensure good mixing, negligible short circuiting and adequate contact time.

Legeron (1982) has demonstrated that high transfer efficiencies of 90-95% may be achieved by a distribution pattern of injected ozone of 40%, 30%, 15%, 15% in a 4-column ozonation system. Reductions in total coliforms from 10^5 $100ml^{-1}$ to less than 1000 $100ml^{-1}$ was achieved by an effective dosage rate of 10 mgl^{-1} ozone and contact times of 11 min and 20s.

3.6.2. Quality of wastewater

As with chlorine, the ozone demand of an effluent is the difference between the applied dosage and the total oxidant residual, which is the concentration of free ozone in the treated wastewater.

Wastewater quality parameters which have the greatest influence on ozonation efficiency appear to be COD and to a lesser extent suspended solids concentration. The decrease in ozone demand with decreasing COD of an effluent was demonstrated by Stover and Jarnis (1980), who found that a 5-10 mgl^{-1} dose was necessary to achieve 70 total coliforms 100 ml^{-1} in filtered nitrified effluent compared with 15-20 mgl^{-1} in filtered secondary effluent. The corresponding increase in dose with COD levels in secondary effluent was also observed by Gomella (1977) with progressively higher ozone doses required to achieve a 4 log reduction of total coliforms (Table 3.4).

Filtration is a means of improving disinfection efficiency through a reduction in COD rather than suspended solids. Solids are easily removed via oxidation and solubilisation, and COD and nitrite levels have been considered more important in ozone consumption (Gan *et al*, 1977). However, in complete contrast, Legeron and Girardin (1981) reported that the suspended solids concentration was important, and that variations in soluble COD had virtually negligible effect on disinfection efficiency for domestic effluents.

Table 3.4: Ozone doses necessary to achieve a 4 log reduction in total coliforms in wastewaters with varying COD (Gomella, 1977)

Effluent quality	COD (mgl^{-1})	O_3 dose (mgl^{-1})	Residual (mgl^{-1})
Non filtered activated sludge	30-44	5.2	0.11
	46-68	9.1	0.3
	72-104	11.6	0.5
Sand filtered activated sludge	30-44	4.0	-
	46-68	7.0	-
	72-104	9.0	-

Whilst the 'all or nothing' concept of ozone disnfection, in which a certain threshold of ozone dosage must be reached before disinfection takes place, is not accepted by some researchers (Nebel *et al*, 1976; Evison, 1978), there is evidence to suggest that the initial ozone demand of the wastewater must be satisfied before effective disinfection can occur (Rakness and Hegg, 1985). Although a powerful oxidant such as ozone is unlikely to selectively oxidise organics without simultaneous disinfection, the latter may not be apparent in the first instances of the reaction.

In an evaluation by Rakness *et al* (1984) of disinfection performance of an ozonation plant at Vail, and a chlorination plant at Avon, Colorado, it was found that a 1 log reduction of faecal coliforms could be achieved in both cases at a transferred dose of $1.7 mgl^{-1}$. However, extrapolation to the intercept of the curves at the 100% survival ratio illustrated a transferred ozone dosage of $0.79 \ mgl^{-1}$ is required before effective disinfection occurs. this value is 2-6 times higher than the equivalent value for chlorine. This is belived to be due to the higher reactive properties of ozone, which must satisfy the oxidant demand reactions.

Ozone has an important advantage over chlorine in that ammonia levels have little effect on its disinfection efficiency. Though it reacts rapidly with ammonia at high pH, through a free radical mechanism, direct oxidation at normal pH is considered insignificant. Carbonaceous materials tend to be oxidised in preference to ammonia and amines (Rice *et al*, 1981). Experiments on nitrified wastewater confirmed that the degree of nitrification had little effect on ozonation efficiency (Den Blanken, 1985).

The pH of the wastewater is significant in that disinfection is enhanced by the slower direct oxidation which occurs at lower pH (< 8.5). Ozone is consumed only slowly by organics and a longer lasting residual is obtained (Farooq *et al*, 1977; Duguet *et al*, 1987). However, pH is not considered significant as long as a constant residual is maintained (Duguet *et al*, 1987). Pilot testing is the most reliable indicator of ozone demand and is essential for wastewaters which exhibit a high and unpredictable demand.

3.6.3. Contact Time

The oxidising potential of ozone is immediately available once it is in solution, unlike chlorine which undergoes a preliminary hydrolysis step. However, a measurable ozone residual cannot be established until the effluent ozone demand has been satisfied. Although the action of ozone is rapid, contact times should be of the order of several minutes to permit adequate disinfection since the process is limited by the rate of mass transfer. At wastewater ozonation plants in the US, contact times are of the order of 10 min.

In wastewater ozonation, ozone is usually applied in stages to avoid short circuiting which may occur in a single stage dose. An adaption of potable water treatment maintains 4 contact tanks in series with the first 3 designed to achieve a reduction in COD with contact time of 20-30 min, whilst the fourth tank maintains a residual of $0.4gm^{-3}$ for 4 min to effect disinfection (Richard, 1986). Due to the long contact times and high ozone demand of wastewater, high doses of 15-20 mgl^{-1} are necessary.

A shorter contact time (ie 5-10 min) may prove more effective when reductions in COD are not critical, such that desired reductions in coliforms are achieved without excessive consumption of ozone in competing demand reactions. The contact time should be adjusted accordingly to the desired disinfection target and pilot testing is highly recommended to determine the optimum contact time.

3.7 Toxicity and by-product formation

3.7.1 Residual toxicity

Ozone is an extremely toxic gas but in wastewater treatment it is likely that any residual will be quickly degraded in the receiving waters.

In a comparison of the toxicity of municipal secondary sewage effluent following chlorination, dechlorination and ozonation, the lethal sensitivity to a variety of fish and invertebrate species was determined (Arthur *et al*, 1975). The chlorinated effluent was found to be appreciably more toxic than the ozonated or the dechlorinated effluent with 7d LC_{50} ranging from 0.08-0.26 mgl^{-1} for fish and 0.21-0.81 mgl^{-1} for invertebrates. Lethal residual levels of ozone to fathead minnows was found to be 0.2-0.3 mgl^{-1}. Long term tests on survival and reproduction of fathead minnows, amphipod *Grammaris pseudolimnaeus* and the water flea *Daphnia magna* indicated no difference between non-disinfected and ozonated effluent. This was in contrast to chlorine, which significantly affected spawning and reproduction success.

A pilot plant study to determine the toxicity of effluents disinfected with ozone, chlorine and bromine chloride also found that ozonised effluent showed no detrimental effects upon the survival of fathead minnows. Acute toxicity tests showed a lower mortality rate with ozone than the alternative disinfectants, though this may have been affected by the fact that the ozone effluent was filtered prior to disinfection (Ward *et al*, 1977).

However in contrast to these studies, an evaluation by Meldrim *et al* (1981) of the effects of ozonated and chlorinated condenser discharges on the white perch *Morone americana* indicated that the toxic effects of the two disinfectants was influenced by the degree of salinity in the receiving water. At salinities between 0.5-2.5 gkg^{-1} the biological effects of ozone were less severe than those of chlorine whilst results of the toxicity tests in freshwater indicated the reverse. In estuarine water the ILC_{50} (96, 2) (96 h LC_{50} for 2h intermittent exposure) for chlorine with white perch was approximately 0.1 mgl^{-1} but no mortality occurred with ozone, even at the highest concentration of 0.66 mgl^{-1}. Behavioural studies showed that white perch avoided average concentrations of 0.07 mgl^{-1} ozone and 0.04 mgl^{-1} total chlorine, both of which are sub-lethal levels. In the freshwater system however, the ILC_{50} (96, 2) for ozone was 0.28 mgl^{-1} compared to 0.73 mgl^{-1} chlorine. Avoidance response studies showed that 0.11 mgl^{-1} ozone evoked a response in perch whilst 0.2 mgl^{-1} chlorine was tolerated.

Though these studies were conducted on waters at a higher temperature than that typical of sewage, an inverse relationship between temperature and ozone toxicity was strongly suggested. The difference in response of the two aquatic systems was thought to be due to the different oxidation by-products arising from chlorine and ozone.

In general, toxicity to freshwater fish appears to begin at residual concentrations of 0.001 mgl^{-1} with gill damage and loss of equilibrium. However unless the concentration reaches 0.01 mgl^{-1} (which causes 50-100% mortality), most fish should recover if ozone is dissipated from the wastewater. The larvae of most species of fish appear more sensitive than the eggs with adverse effects noted at residual concentrations of 0.1 mgl^{-1} and 1 mgl^{-1} respectively. Ozone residuals of 0.01 mgl^{-1} can also cause mortality in freshwater invertebrates (Hubly *et al*, 1985).

The time dependent nature of the toxicity of chlorine and ozone means that site-specific, sub-lethal effects may be more useful in evaluating disinfection impact than toxicity data; in which case the most likely environmental effect from the use of ozone would be loss of habitat. However, ozonated effluent may also improve the aquatic environment by the addition of dissolved oxygen.

The effects of residual ozone, though it is demonstrably toxic, are no greater than those of residual chlorine. However, ozone decomposes much more rapidly (WPCF, 1986), with a half-life of 20-30 min in distilled water (Miller *et al*, 1978; Hubly *et al*, 1985), thus it is likely that it will dissipate before any adverse effects can occur.

3.7.1 By-product formation

Ozone oxidises a wide range of organic compounds but the reaction products and mechanisms are not generally well documented.

Ozone reactions involve direct oxidation with ozone or indirect reactions with radical species such as OH, depending on the pH of the solution and the presence of chain initiators in solution. In general, ozone by-products tend to be more polar and the addition of oxygenated functional groups to previously non-biodegradable compounds may produce sites for microbial attack such as in the oxidation of cyanide to cyanate. The conversion to more biodegradable and thus more water soluble products may remove the potential for detection, but the subsequent fate of ozonated by-products and their potential health risk remains to be properly assessed.

Experiments on drinking water by Lykins and Koffskey (1986) revealed that ozone reduced total organic carbon (TOC) slightly and total organic halogens by almost half and non-volatile organics by 11 - 84%. Compounds which showed an increase were total alkaldehydes, octanal and nonanal.

The production of aliphatic aldehydes and alkanes in wastewater ozonation at Estes park, Colorado, was reported by Sievers *et al* (1978), whilst in some samples toluene was also produced. Precursors were thought to be non-volatile as there were no corresponding decreases in the chromatographic peak sizes of the volatile components. An examination of a biologically treated wastewater after ozonation (Legube *et al*, 1987) showed an increase in alcohols, aldehydes, short chain fatty acids and some alkanes and aromatics which was in agreement with laboratory studies of the specific organic compounds. Quantification of the identified organics showed only 10-15% of the potential organics had been considered. The increase in alkanes was thought to be due to partial oxidation of macro-molecules or colloidal particles and an increase in amino acids due to attack of proteins and polypeptides present in the secondary effluent. The major part of the TOC was in the form of both high and low molecular weight biological compounds such as combined amino acids and humic substances.

A number of experiments have been conducted on specific compounds likely to be present in wastewaters. Studies by Elmghari-Tabib *et al* (1982) found that concentrated solutions of alcohols reacted with ozone to produce aldehydes, ketones, acids and peroxycyclic products, whilst amines reacted to produce hydroxylamine oxime and amides. In dilute solutions the compounds disappeared and the reactions of amines did not proceed to the condensation phase. The reactions of 2-propanol, acetic acid and oxalic acid were investigated by Powell *et al* (1977), who observed glyoxylic, oxalic, formic and acetic acids as common end products, prior to their complete oxidation to carbon dioxide.

Studies into the effects of ozone on humic acids, naturally occurring in high concentrations in wastewaters, have found that the resulting compounds have a lower molecular weight with increased acidic properties and are more biodegradable (Maier, 1982). An investigation by Killops *et al* (1985) into ozonation of humic and fulvic acids found that it had only a minor effect on the amounts and types of volatile organics identified, suggesting little oxidation of polymeric humic substances. However an increase in aliphatic fatty acids, benzene diacids and diacids was noted after ozonation of humic acids, whilst analysis of fulvic ozonated by-products was complicated by the high proportion of poly-functional compounds which increased after ozonation.

Whilst most ozonated by-products have no deleterious health effects and are simply those which would be produced following environmental oxidation of natural organics, the exception to this is the formation of certain aldehydes and undetected hydroperoxides. Some aldehydes are known to be severe hepatotoxins. Unsaturated aldehydes or enals are particularly reactive with some biological molecules and have been shown to block both protein and DNA synthesis. Aldehydes generally diffuse and are adsorbed easily, so that effects may be observed some distance from the site of generation or administration (Glaze, 1986).

In a comparative study of wastewater disinfection with chlorine, ozone, or UV it was concluded that ozone both destroys and produces non-volatile organic constituents including mutagenic constituents (Jolley *et al*, 1982). Volatile organic micropollutants were not considered in this study. With increasing ozone dosage, the number and quantity of ozone-produced constituents was observed to reach a maximum then decrease. Although ozonation would ultimately destroy most of the constituents the required ozone dosage would be much greater than normally encountered in wastewater disinfection. It was clear from this study that mutagenic micropollutants can occur in wastewater effluents before disinfection, but disinfection by ozone can lead to an increase in the number of mutagenic materials present in these effluents.

Although ozone does not produce THMs directly and is employed to destroy the various precursors, it has been postulated that once a plateau of THM precursor destruction in natural waters is reached, most of the remaining ozone is subsequently used in forming THM precursors (Glaze, *et al* 1982). In addition, ozone is known to oxidise bromide ion to hypobromous acid (HOBr) and subsequently bromate, which may result in brominated THMs and other organic by-products if ozonated effluent is discharged to the sea (Glaze, 1986).

Ozone reactions in wastewater are obscured by the complex matrix of precursors in the effluent, together with analytical limitations in identifying water soluble products. In general ozone tends to be more reactive to those compounds which have unsaturated linkages such as alkenes and aromatics or which are activated to electrophilic substitution such as phenols and aromatic ethers (Glaze, 1986). Studies on ozonation of wastewater appear to indicate an increase in aldehydes, alkanes, alcohols, aliphatic fatty acids and aromatics. Though no adverse health effects will be expected with the majority of these by-products, certain compounds such as enals and hydroperoxides give rise to concern. However, there is insufficient evidence at the present time to allow quantification of the risk.

It was concluded by Hubly *et al* (1985) that ozonated by-products would be produced in such small quantities (ngl^{-1}) in wasttewater effluents that the human exposure risks are negligible. Dilution of these products in the receiving waters results in an even lower risk. Since the toxic dose-response levels for ozonated by-products are orders of magnitude higher than expected effluent levels, adverse effects to aquatic organisms are not considered likely to occur.

3.7.3 Oxidation of organics

Whilst the formation of ozonated by-products is largely undesirable, the use of ozonation to oxidise certain harmful organics is well established. The process of using ozone for cyanide destruction on an industrial scale has been practised for many years. Nebel *et al* (1976) found that 6 mgl^{-1} ozone was sufficient to destroy all naturally occuring cyanide in secondary effluent. The cyanide is oxidised to the cyanate ion CNO^- which is non-toxic and readily destroyed in acid or alkali. Ozone has also been used for the removal of phenols from industrial effluents since the late 1960s. In 1971 the Electricity Council investigated the reactions of a wide variety of phenolic substances and found small doses of ozone reduced concentrations significantly (Hillis, 1971). The end products tend to be unsaturated aliphatic diacids or aldehydro acids which are non-toxic and biodegradable. Ozone is also used for the removal of colour, through the breakage of conjugated double bonds normally associated with coloured compounds.

The efficacy of ozonation and chlorination for the removal of EPA priority pollutants was investigated by Lee and Hunter (1985), who found that phenols and polynuclear aromatics were particularly susceptible to attack by ozone, whilst halogenated dienes, ethenes and propenes are also fairly readily degraded. The halogenated alkanes were considerably more resistant to degradation as were the phthalate esters.

Pilot studies conducted by Thames Water in 1982, used ozone in conjunction with GAC for the removal of trace organic compounds from river waters containing significant quantities of treated sewage effluent.

3.8 Laboratory and pilot studies

3.8.1 Colchester (Ozotech/Anglian Water)

In 1987, in conjunction with Anglian Water, Ozotech conducted experiments to establish the bactericidal efficiency of ozone in wastewater. Experiments were conducted on final effluent; high level crude (mainly domestic); low level crude (including a significant volume of trade effluent); and primary settled sewage, with varying ozone doses and contact times. The inactivation efficiencies for *E.coli*, faecal streptococci and coliforms in addition to BOD and COD reductions were tabulated.

Preliminary laboratory results indicated that bacterial reductions were highly variable in untreated sewage and only at the higher contact times were significant reductions achieved. High COD levels in the crude effluents may have accounted for the generally lower reductions in bacteria, although in the settled sewage neither significant reductions in bacterial numbers or COD/BOD were obtained. Results on final effluent were more consistent and showed that an ozone dose of 17 mgl^{-1} and contact time of 10 min could achieve a 3 log reduction in *E.coli*. Further pilot studies have been postponed.

3.8.2 Meurthe et Moselle (Joret *et al*, 1982)

All operational wastewater ozonation plants currently operate on high quality wastewater which has received secondary or tertiary pretreatment.

In one of the few pilot studies conducted using untreated sewage (Joret *et al*, 1982), the rate of inactivation of faecal bacteria and enteric viruses was compared as a function of applied ozone dose. Raw wastewater was chosen to ensure a detectable level of enteric viruses and to reproduce the protective rôle of suspended matter that is found in practice.

The wastewater characteristics are shown in Table 3.5. Four assays were carried out using a porous diffuser ozonator and an average wastewater flow rate of $0.04m^3h^{-1}$ and contact times of 2 min 40s, 11 min and 19 min. Ozone doses of 2.2 - 4.1 mgl^{-1} were required to achieve residuals of 0.06 - 0.35mgl^{-1} at a contact time of 19 min. Inactivation curves were calculated in relation to the injected ozone dose (Table 3.6); the steeper the curve, the more susceptible the microorganism to ozonation. These show that viruses were more resistant than faecal bacteria while *E.coli* and faecal streptococci were equally sensitive to ozone. Thus a dose of 2.5 mgl^{-1} ozone at 19 min contact time corresponded to a 1.7 log reduction in *E.coli*, a 1.9 log reduction in faecal streptococci and a 1.1 log viral reduction. The increased resistance of viruses was attributed to their tendency for

Table 3.5: Characteristics of wastewater used in ozone pilot studies on urban sewage at Meurthe et Moselle (Joret *et al*, 1982).

Parameter	Value
pH	7.5 - 8.5
SS (mgl^{-1})	85 - 116
COD (mgl^{-1})	100 - 240
Temp °C	16 - 20
E.coli (100ml^{-1})	2.4 - 3.7 x 10^6
faecal streptococci (100ml^{-1})	2.4 - 4.1 x 10^5
Virus (l^{-1})	20 - 156

Table 3.6: Ozone inactivation curves for indigenous raw wastewater microorganisms after 19 min contact time (Joret *et al*, 1982).

	Inactivation curve slope				
Assay	1	2	3	4	Average
E.coli	-0.85	-0.51	-0.71	-0.69	-0.69
Faecal streptococci	-1.02	-0.53	-0.71	-0.73	-0.74
Virus	-0.45	-0.49	-0.43	-0.38	-0.43

aggregation affording a greater degree of protection. Ozone seemed to be ineffective for short (2 min) contact time but the longer contact times gave similar results such that there was no linear relation observed between bacterial inactivation and contact time. A weak correlation was observed between bacterial inactivation and wastewater load (SS and COD) suggesting that the wastewater ozone demand was competing with disinfection efficiency, though no such correlation was found for enteric viruses. The results appeared to indicate generally enhanced disinfection efficacy at the higher residual ozone levels.

At best, the maximum inactivation efficiency which could be achieved on raw wastewater was a 3 log reduction in *E.coli* with an ozone dose of 2.5 mgl^{-1} for a 19 min contact time. However, in comparison with results for treated effluents, the data presented in the study showed that ozone inactivation efficiency for raw wastewaters was generally low. This was thought to be related to the higher organic matter content and hence competition from oxidation demand, and the protective effect of solids.

3.9 Full scale operation

Current operational wastewater facilities in the US using air and oxygen as a feed-gas are summarised in Tables 3.7 and 3.8 respectively (Robson, pers.comm.). Out of a total of 36 existing facilities, 8 out of 22 air-ozone plants and 11 out of 14 oxygen-ozone plants are still in operation. In addition there are three new facilities at West Knoxville, Tennessee (3785 m^3d^{-1}); El Paso, Texas (37850 m^3d^{-1}); and Cleveland, Ohio (190,000 m^3d^{-1}). There are also two wastewater ozonation plants in France at Guêthary (1650 m^3d^{-1}) (Fressonnet-Chambarlhac *et al* 1983b) and St Michel en Grèves (375 m^3d^{-1}). The past reputation for poor perfomance of ozonation facilities in the US was largely the result of undersized air preparation plants and poor ozone contactors.

Table 3.7: US wastewater ozonation facilities using air as feed gas (Robson, pers.comm.).

Plant Location	Design Flow		Ozone Generator				Start-up Date	Status
	m^3 day^{-1}	US mgd	Type	Number	Capacity/Units $(kghr^{-1})$	(lbd^{-1})		
Indiantown, FL	1,893	0.5	V/W/L	1	1.10	58	1975	NOE
Woodland, TX	5,678	1.5	H/W/L	1			1976	ABAN
Estes Park, CO	5,678	1.5	H/W/L	2	1.43	76	1977	NOT
Herriman, NY	22,722	6.0	V/D/H	2	1.32	70	1977	NK
Chino Basin, CA	18,927	5.0	H/W/L	3	4.63	245	1877	IO
Palo alto, CA	15,142	4.0	H/W/L	1	1.13	68	1978	NK
Collegeville, MN	833	0.22	NK	NK	NK	NK	1978	NK
Hunter Highlands, NY	3,785	0.03	V/D/H	2	0.04	2	1978	NK
Cotter Gasville, AR	3,785	1.0	H/W/L	2	1.93	102	1978	IO
Oak Ridge, NY	454	0.12	V/D/H	2	0.79	42	1980	IO
Morton AFB, CA	946	0.25	NK	NK	NK	NK	1980	IO
Carmel, NY	3,785	1.0	NK	NK	NK	NK	1980	IO
Potomac Heights, MD	757	0.2	H/W/L	1	0.45	24	1980	ABAN
Hercules, CA	1,514	0.4	H/W/L	1	0.96	51	1980	NK
Marion, NY	473	0.125	H/W/L	1	0.36	19	1980	NK
Brookings, SD	22,716	6.0	H/W/L	2	2.36	125	1980	ABAN
Delaware City, OH	5,678	1.5	V/D/H	2	1.61	85	1981	IO
Frankfort, KY	26,498	7.0	H/W/L	3	3.78	200	1980	IO
Yaphank, NY	454	0.12	V//H	2	0.65	35	1980	NK
Granby, CO	3,785	1.0	V/D/H	2	0.52	28	1981	ABAN
Vail, CO	30.283	8.0	H/W/L	2	2.36	125	1982	IO
Twining, NM	360	0.10	NK	NK	NK	NK	1983	NK

NOTES:

V/W/L - Vertical tube/water cooled/low frequency
H/W/L - Horizontal tube/water cooled/low frequency
V/D/H - Vertical tube/dual cooled/high frequency
NK - Not Known

IO - In Operation
NOE - Not in operation for economic reasons
NOT - Not in operation for technical reasons
ABAN - Abandoned

Table 3.8: US wastewater ozonation facilities using oxygen as feed gas (Robson, pers.comm.).

Plant Location	Design Flow		Ozone Generator				Start-up Date	Status
	m^3 day^{-1}	US mgd	Type	Number	Capacity/Units (kgh-1)	(lbd^{-1})		
Mahoning Valley, OH	15,142	4.0	P/A/H	2	3.78	200	1978	IO
Springfield, MO	132,489	35.0	P/A/H	13	5.95	315	1978	IO (1)
Murfreesboro, IN	30,283	8.0	H/W/L	3	3.78	200	1980	IO (2)
Pensacola, FL	75,708	20.0	H/W/L	6	7.56	400	1980	NOE
Concord, NC	94,635	25.0	P/A/H	17	5.16	273	1980	IO (3)
Madisonville, KY	18,930	5.0	P/A/H	3	5.20	275	1980	IO
Holland, MI	32,190	8.5	P/A/H	5	4.73	250	1980	NOE
Ocean City, MD	45,425	12.0	H/W/L	4	9.45	500	1981	IO
Hagerstown, MD	30,283	8.0	P/A/H	5	3.78	200	1982	IO (3)
Rocky Mount, NC	52,996	14.0	H/W/L	4	7.64	404	1982	IO
Olympia, WA	52,996	14.0	H/W/L	3	20.41	1080	1983	IO
Indianapolis, IN								
(Belmont)	454.248	120.0	V/D/H	4	40.20	2127	1983	IO
(Southport)	473,175	125.0	V/D/H	4	40.20	2127	1983	IO
Moorhead, MN	22,710	6.0	P/A/H	2	5.67	300	1983	NOT

NOTES: P/A/H - Plate dielectric/air cooled/high frequency
V/W/L - Vertical tube/watercooled/low frequency
H/W/L - Horizontal tube/watercooled/low frequency
V/D/H - Vertical tube/dual cooled/high frequency

IO - In Operation
HK - Not Known
NOE - Not in operation for economic reasons
NOT - Not in operation for technical reasons
ABAN - Abandoned

NOTES: (1) - Has replaced existing ozone generators
(2) - Will abandon ozone for economic reasons
(3) - Will replace existing ozone generators with another type

3.9.1 St Michel en Grèves (Fressonnet-Chambarlhac *et al*, 1983a)

An ozonation plant was constructed in 1982 to treat effluent from a population of 6000 at St Michel en Grèves, a small seaside resort in Western France. Pretreatment includes screening, grease and grit removal, aeration and clarification, prior to disinfection with ozone and subsequent marine discharge. The ozonation tower has a capacity of $20m^3h^{-1}$ and 55 min contact time but the contact chamber is sized for a future capacity of 900 m^3d^{-1} and 20 min contact time. The characteristics of the ozone generation and contact facilities are shown in Table 3.9.

During the period June-August 1982, a 4 log coliform reduction was obtained in 90% of samples, together with improvement in the effluent quality in terms of colour, nitrite levels and COD, as shown in Table 3.10. The factors affecting inactivation efficiency at the plant have been found to be quality of effluent, contact time, residual ozone and pH. Table 3.11 shows that the effects of increasing COD and NO_2^- in the effluent are lower microbial reductions and residual ozone levels.

3.9.2 Vail, Colorado (ozone from air)

At Vail, Colorado, a wastewater ozonation plant, producing ozone from air, has been in successful operation since October 1982. Despite its higher present worth than a chlorination/dechlorination plant, ozonation was adopted because of its enhanced disinfection properties. Wastewater pretreatment includes coarse screening, grit removal, flow equalisation, activated sludge treatment, submerged contactor nitrification and microscreening prior to disinfection.

Stringent permit standards specify several wastewater quality parameters as well as a monthly average of 6000 faecal coliforms $100ml^{-1}$ and a weekly average of 12000 $100ml^{-1}$. The plant is designed for a peak flow of 30,283 m^3d^{-1} but currently averages

Table 3.9: Characteristics of the ozone generation and contact facilities at St Michel en Grèves (Fressonnet-Chambarlhac *et al*, 1983a)

Effluent tank volume (m^{-3})	Pump capacity (m^3h^{-1})	Ozone generator (gh^{-1})	Contact cycle (m^{-3})	Contact time (min)	Ozone dose (gm^{-3})
230	20	300	4 x 18	54	10

Table 3.10: Characteristics of effluent before and after ozonation, St Michel en Grèves (Fressonnet-Chambarlhac *et al*, 1983a).

		Before Ozone	After Ozone	Abatement (%)
Total coliform	($100ml^{-1}$)	10^6	100	99.99
Fecal coliform	($100ml^{-1}$)	5×10^5	50	99.99
COD	(mgl^{-1})	50	40	20
BOD	(mgl^{-1})	8	6	25
SS	(mgl^{-1})	10	8	20
Colour	($mgptl^{-1}$)	60	6	90
NO_2^-	(mgl^{-1})			50

Table 3.11: Effects of increasing COD and nitrite levels on residual ozone levels and bacterial quality, St Michel en Grèves (Fressonnet-Chambarlhac *et al*, 1983a).

COD (mgl^{-1})	NO_2^- (mgl^{-1})	Ozone (mgl^{-1})	Total coliform ($100ml^{-1}$)	Faecal coliform ($100ml^{-1}$)	Residual ozone (mgl^{-1})
35	0.01	10.4	9	4	0.23
60	0.05	9	93	93	0.1
65	0.05	11	100	12	0.1

at 72,000 m^3d^{-1}, for which a current ozone dosage of 1.5mgl^{-1} is found to achieve target disinfection.

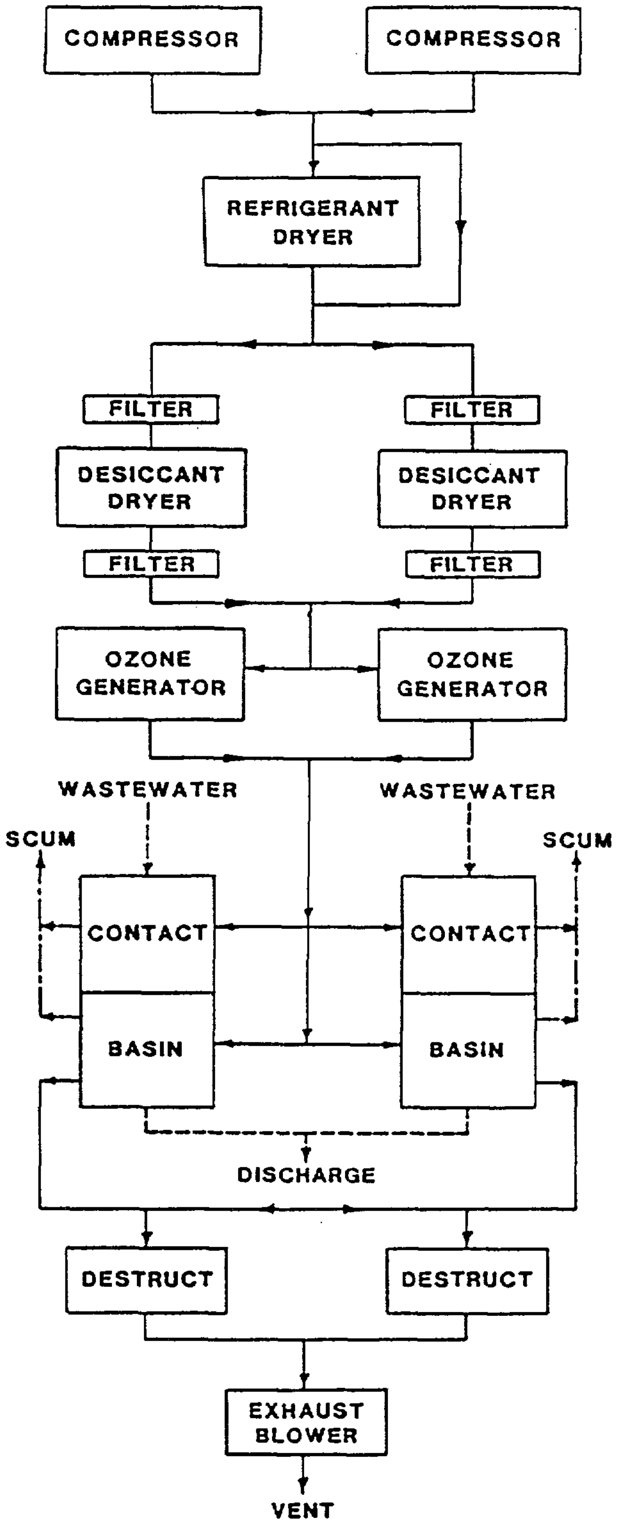
A schematic of the ozone system is shown in Figure 3.2. Two desiccant dryers are designed to provide "dry air" with a dewpoint temperature of -51°C or lower with one tower drying whilst the other tower regenerates the desiccant. Two ozone high voltage water cooled generators (H/W/L) with 126 tube-type dielectrics per unit provide a capacity of 80$gmin^{-1}$ ozone in total. The ozone contactor system comprises two, 2-stage baffled diffusers which provide an average contact time of 22 min with a peak flow contact time of 11 min.

Aproximately 66% of the ozone is directed to the first stage of the contact basin and 33% to the second stage. Two heat-catalyst destruct units which operate at 26-38°C are used to destroy ozone in the off-gas and discharge an ozone concentration of 0.002 gm^{-3} or 0.1 ppm.

The wastewater at Vail is of an extremely high quality (BOD, TSS approximately 6 mgl^{-1}) and disinfection requirements have been consistently met since start-up. Coliform survival was found to be proportional to transferred ozone dosage for a given wastewater quality and a 0.5 - 3 log reduction of faecal coliforms occurred for a transferred ozone dosage of 1 - 8 mgl^{-1}. Effective faecal coliform reduction begins at a transferred dose of approximately 0.79 mgl^{-1}; it was found that discharge permit standards could be met at transferred doses of 1 - 3 mgl^{-1}. Current dosing averages 1.5 mgl^{-1}. The off-gas ozone concentration method for process control was found to give an excellent correlation with faecal coliform survival, and is now used for controlling ozone dosage.

The ozone process at Vail has had reliable operation due to good design features. The air pretreatment facility and contact basin performance are the most critical aspects. A low dosage of 1.5 mgl^{-1} ozone achieves the bacterial permit standards of 6000

Fig 3.2 Schematic of ozone disinfection system at Vail, Colorado (Rakness, Stover and Kreneck, 1983)



faecal coliforms 100 ml^{-1} at a log survival ratio of 0.4-1.0, with off-gas concentration control used to give better control of disinfection performance. In addition, proposed modifications were expected to reduce energy consumption. A plant at Avon with unit processes identical to Vail uses a chlorine/dechlorination system for disinfection. Whilst faecal coliform reductions were equally as effective as in the ozone process, the ozone system was preferred because of chlorine storage safety considerations and the beneficial effect of ozonation on the effluent. Although the ozone system was approximately twice the cost of the chlorine/dechlorination process, both represented a relatively small part of the total plant costs (4.5-7% of capital costs).

3.9.3 Indianapolis (ozone from oxygen)

There are currently two wastewater ozonation plants in Indianapolis, Indiana, using oxygen as a feed gas; the Belmont plant and the Southport plant. Both are designed for a wastewater flow of approximately 450,000 m^3d^{-1}. Initial problems with the plants included excessive dielectric breakage, potential for fire in the ozone destruct unit and periods of low gas flow through the ozone generators. Following modifications in 1983, successful ozone disinfection was achieved on a continuous basis, and performance and operation was evaluated in 1986 by Rakness *et al* (1986).

Pretreatment at each plant involves primary clarification, bioroughing towers, oxygen activated sludge, nitrification and tertiary filtration. The ozone is generated from oxygen which is then recycled and used in the nitrification system, whilst the excess ozone in the off-gas is destroyed by a heat-catalyst unit.
Ozone is generated by four high frequency, "dual cooled" dielectric units with a capacity of 669 $gmin^{-1}$ each, and transferred to the wastewater by means of a fine bubble diffuser. Design criteria for the two ozonation systems is shown in Table 3.12. The average design flow at both plants is 329 m^3min^{-1} with an ozone dosage

Table 3.12: Design criteria for the Belmont and Southport ozonation systems (Rakness *et al*, 1986)

Wastewater flow		
Peak design	(m^3min^{-1})	394
Ave design	(m^3min^{-1})	329
Ozone generation		
Concentration	(gm^{-3})	29
Production	($gmin^{-1}$)	2,0007
Applied dose peak	(mgl^{-1})	5.1
Applied dose ave	(mgl^{-1})	6.1
Ozone facilities		
Number		4
Capacity (each)	($gmin^{-1}$)	669
Dielectrics (each)	112	
Ozone contact basin		
Type		fine bubble
number of basins		4
Stages		4

Table 3.13: Performance of ozonation systems at Belmont and Southport (Rakness *et al*, 1986).

		Southport	Belmont
Influent			
Flow	(m^3min^{-1})	229.2	246.0
COD	(mgl^{-1})	42.1	51.4
Faecal coliform	($100ml^{-1}$)	3,857	5,859
Effluent			
COD	(mgl^{-1})	39.6	49.3
Faecal coliform	($100ml^{-1}$)	67	132
Operating			
Applied dosage	(mgl^{-1})	3.45	4.54
Transfer efficiency	(%)	87.3	-
Detention time	(min)	19.8	18.5
Ozone production	($gmin^{-1}$)	750	1,024

of 6.1 mgl^{-1}; however both plants are currently operating at lower than design production rates. The wastewater flow is less than design because both plants are new, but the applied ozone dosage is lower because plant effluents are of higher quality than anticipated.

During the 1986 disinfection period, both plants consistently met the permit weekly limit of <400 faecal coliforms $100ml^{-1}$. Though the influent faecal coliform concentration was higher at the Belmont Plant, the faecal coliform reduction was slightly better at the Southport plant.

This was thought to be due to the higher COD at Belmont which could result in a greater ozone demand. Table 3.13 indicates that an applied dose of 3.45 mgl^{-1} at Southport achieves a 1.8 log reduction in faecal coliforms whereas a dose of 4.54 mgl^{-1} at Belmont achieves a 1.6 log reduction.

3.10 Costs

Ozone disinfection is generally more costly than other operational disinfection systems.

3.10.1 Capital Costs

Pilot plant studies by the USEPA on waste water ozonation shows that 36% of the cost of ozone disinfection is amortisation of the fixed capital investment (Rice *et al*, 1981). The capital cost components include:

ozone generation system
contactor
ozone plant housing
pump house and plant.

The costs of ozonation systems demonstrate economies of scale with data from installed ozone systems in both water and wastewater plants in the U S showing costs of approximately £1350 $kg^{-1}d^{-1}$ (at a production rate of 4.5 kgd^{-1}) and £520 $kg^{-1}d^{-1}$ (at 45.36 kgd^{-1}) (Rakness, pers.comm.). The cost of ozone contacting is comprised primarily of the cost of a covered concrete basin which can be determined from standard engineering cost estimates. The detention times generally range from 10-20 min at operational US wastewater plants. The housing cost tends to vary accordingly to location and type of construction.

Using the criterion that most rooms which house ozone equipment, including air treatment and auxillary equipment have 0.17-0.30 m^2 per kgd^{-1} of generation equipment; this may be used as an initial sizing estimate to obtain local construction costs (Rakness, pers.comm.).

3.10.2 Operating Costs

Ozone production involves a number of energy requirements and electrical consumption is typically 60-80% of operation and maintenance costs (Rakness and Hegg, 1985) or approximately 17% of total costs (Rice *et al*, 1981). A breakdown of the sources of energy consumption for an air-feed ozone system at Vail, Colorado is given below, with the percentage energy consumption in parentheses:

generation of ozone (30% energy consumption)
provision of cooling water to generator (5%)
air treatment, desiccant dryer (12%)
dissolution of ozone using bubble diffuser (49%)
destruction of ozone in off gas using heat/catalyst (2%).

As shown, the majority of energy is required for ozone generation and dissolution. The ozone generation electricity consumption is proportional to the ozone production rate, whilst the fixed power demand of the auxiliary equipment means a higher consumption, per kg ozone produced,is observed at the lower ozone production rates.

There is limited information in the literature on the costs of oxygen-fed ozone plants, although Legeron (1982) reported that twice as much ozone may be produced for an equivalent electricity consumption and the same investment in ozone generation equipment. Energy consumption was reported as approximately 20 kWh kg^{-1} ozone from air and approximately 10 kWh kg^{-1} ozone from oxygen.

In terms of maintenance and manpower requirements, a wastewater ozonation plant at Vail, Colorado, operating with an average ozone production rate of 7.5 g min^{-1} , required an estimated at 0.25 man-years to perform daily operation checks, clean the dielectrics annually and to maintain equipment. The US EPA studies estimate operating labour at 0.5 man years, which represents approximately 16% of total costs (Rice *et al*, 1981).

3.10.3 Total costs

The hourly flow of effluent from the plant at St Michel en Greves (Section 3.9.1) was extrapolated and the costs calculated for an average and maximum annual flow. The costs are presented in Table 3.14 and show that the amortised capital costs per m^3 are of the order of 5-9 pm^{-3} whilst operating costs (primarily power and maintenance) are 2-3 pm^{-3}. These costs are on a 1982 price basis and assume a conversion rate of £1 = 10.1 FF. Experience has shown that costs can be reduced by shorter contact time and lower doses to achieve the same ozone residual leading to lower civil engineering, equipment and electricity costs.

A summary of the costs for the Vail ozonation process (Section 3.9.2) is given in Table 3.15. The capital cost for the ozone disinfection system includes the cost of the ozone generation equipment, contact basin and a portion of the building which houses the units. The system was sized to meet peak demand and cost in 1983 an estimated $450,000 (approximately £250 000) which was 6.8%

Table 3.14: Capital and operating costs calculated for a full scale ozonation plant at St Michel en Grêves (1982 price basis) (Fressonnet-Chambarlhac *et al*, 1983a)

	Total (FF)	Amortised (FFy^{-1})	Average flow cost (FFm^{-3})	Max flow cost (FFm^{-3})
Capital				
Civil Eng	200,000	20,000	0.27	0.15
Equipment	350,000	45,000	0.60	0.33
Total	550,000	65,000	0.87	0.48
Operating				
Maintenance	(at 10,000 FFy^{-1})			0.13 0.07
Electrical	(at 0.275 $FFkWh^{-1}$)		0.17	0.17
Total	(FF m^{-3})		0.30	0.24
	(p m^{-3})		3.0	2.4

Hourly flow = $20m^3h^{-1}$
Daily flow = $375m^3d^{-1}$
Annual flow = 200 x 375 = $75,000m^3y^{-1}$ (ave)
= 365 x 375 = $137,000m^3y^{-1}$ (max)

Ozone processes use 0.60 $kWhm^{-3}$

Table 3.15: Capital and operating costs for a full scale ozonation plant at Vail, Colorado (1983 price basis) (Rakness *et al*, 1984)

Wastewater Flow	
Design Ave	7.1 m^3min^{-1}
Design Peak	14.2 m^3min^{-1}
Current Ave	5.0 m^3min^{-1}
Ozone Dosage	
Design Peak	5.6 mgl^{-1}
Current	1.5 mgl^{-1}
Ozone Generation	
Design Peak	90 $gmin^{-1}$
Current	7.5 $gmin^{-1}$
Capital Cost	
Ozone Process	\$450,000
1. generation equipment	\$250,000
2. contact basin	\$100,000
3. building	\$100,000
Operating Cost	
Ozone Process	
1. electrical (5.5 ¢kWh^{-1})	\$5,420 y^{-1}
2. maintenance	\$2,900 y^{-1}
	0.10 ¢m^{-3}
3. manpower (\$25,000 y^{-1})	\$6,250 y^{-1}
	0.24 ¢m^{-3}
subtotal	\$14,570 y^{-1}
(¢m^{-3})	0.55
(pm^{-3})	0.3

Table 3.16: Capital and operating costs for the Belmont and Southport ozonation plants (Rakness *et al*,1986).

	Belmont	Southport
Capital		
Ozone disinfection	$4,711,000 combined	
Operation and Maintenance		
Electrical	$114,329	$ 92,718
Operations labour	$108,976	$108,976
Maintenance labour	$ 35,177	$ 35,706
Supplies	$ 50,327	$ 18,201
	$308,809	$255,601
	0.24 ¢m^{-3}	0.21 ¢m^{-3}
	0.14 pm^{-3}	0.12 pm^{-3}

of total plant cost. The operating cost includes electrical, maintenance and manpower costs estimated at \$14,570 y^{-1} (£8000 y^{-1}) or 0.55¢ m^{-3} (0.3 pm^{-3}), which is 3.1% of total plant operation and maintenance cost.

Capital costs for the plants at Belmont and Southport, Indiana (Section 3.9.3) arise from the ozone generation equipment, equipment housing and ozone contact tank. The ozone disinfection system was sized to meet peak operating conditions. Operation and maintenance costs are based on electricity consumption, operation labour, maintenance labour and maintenance supplies. The costs, on a 1986 price basis, are summarised in Table 3.16.

3.11 Conclusions

1 Ozone is an efficient microbicide characterised by its fast action and the low concentrations required. Although more efficient as a bactericide than a virucide, overall it is more effective than chlorine. Faecal coliform reductions of 3-4 log may be achieved with a 5-10 mgl^{-1} dose in secondary effluents, whilst wastewaters with a higher COD load require higher doses of 15-20 mgl^{-1}.

2 Wastewater requires extensive pretreatment to avoid excessive ozone consumption in chemical demand reaction at the expense of disinfection. Currently operational wastewater disinfection plants in France and the US operate on high quality secondary and tertiary effluents, which adds significantly to the overall costs.

3 Ozone disinfection is more costly than alternative operational disinfection systems largely due to the generating equipment costs (capital) and power costs (operating). Certain ozone facilities in the US were abandoned due to the excessively high operating and maintenance costs.

4 There is no residual toxicity as ozone is short-lived and dissipates rapidly. Although the ozonated effluent is not thought

to have any deleterious environmental impact on the receiving water, the possible formation of epoxides and enals gives cause for concern and warrants an assessment of their likely impact. Several years operating experience at wastewater plants have failed to detect any serious consequences of ozonation; on the contrary, additional benefits such as an increase in dissolved oxygen and reductions in COD, BOD, colour and odour have been reported.

5 Ozone is generated on-site which eliminates any transportation risks. Although it can be detected at very low concentrations below the safety threshold, it is nevertheless very toxic and adequate safety precautions must be taken.

6 Ozone production is a highly technical process requiring complex and costly equipment. Past difficulties which have occurred at operational plants in the US and France were largely due to underdesign of the air preparation systems and mis-specification.

4 ULTRA-VIOLET RADIATION (UV)

4.1. Introduction

The bactericidal properties of UV light were first recognised in 1877 but its commercial application was dependent on the development of the mercury vapour lamp in 1901 and the introduction of the quartz sheath to buffer against temperature differences. UV was not initially adopted for large-scale disinfection because of its high operating costs and maintenance problems, coupled with the fact that it fails to provide a disinfection residual. However, increasing concern over possible toxic effects associated with the use of chlorine in wastewater disinfection provided a major impetus in the development of alternative methods in the US. This, together with the development of cheaper and more efficient UV sources, led to its increasing application.

In 1984, 53 operational UV systems for disinfecting municipal wastewater were identified in the US and Canada with 64 in the design or construction phase (White *et al*, 1986). These facilities, with flow capacities ranging from 2.7 m^3d^{-1} to 2.2 m^3s^{-1} operate successfully on secondary effluents. In order for UV to be effective the light must be absorbed by microorganisms, which is the major limiting factor in wastewater application where high concentrations of solids and ionic salts can absorb the light and/or protect by encapsulation. Pilot studies conducted on lower quality wastewaters suggest economic rather than technical considerations mitigate against the full scale implementation of UV.

4.2 Production and application

4.2.1 Lamps and units

UV light is generated by the electrical discharge of metal vapour; mercury lamps are used in commercial applications.

These may be either low pressure lamps which emit approximately 92% of their light at 254 nm, or medium pressure lamps which have a much higher current. The higher mercury vapour pressure in medium pressure lamps leads to a typically diffuse spectrum. The advantage of the medium pressure lamp is that a higher dose can be achieved for a given flow rate, which also simplifies the configuration of the system. However, this is offset by the higher cost and shorter operating life. The characteristics of low and medium pressure lamps are shown in Table 4.1.

UV lamps are long thin tubes (generally 0.9 and 1.6m long, diameter 1.5-2.0cm) with the active portion or arc typically 0.75 or 1.5m long. The radiation intensity is approximately constant along a segment of a straight line parallel to the tube axis and the nominal UV output is typically 18.2 Wm^{-1} of arc (Scheible, 1987). There are two basic generic designs for UV reactors, which both separate the lamps from the wastewater and buffer against any temperature changes:

a) The contact reactor, in which the lamps are encased in quartz sleeves, only slightly larger in diameter than the lamp itself, and are submerged in water.

b) The non-contact reactor, in which the lamp is suspended around the outside and parallel to thin-walled fluorocarbon polymer tubes that carry the wastewater.

4.2.2 Reactor configuration

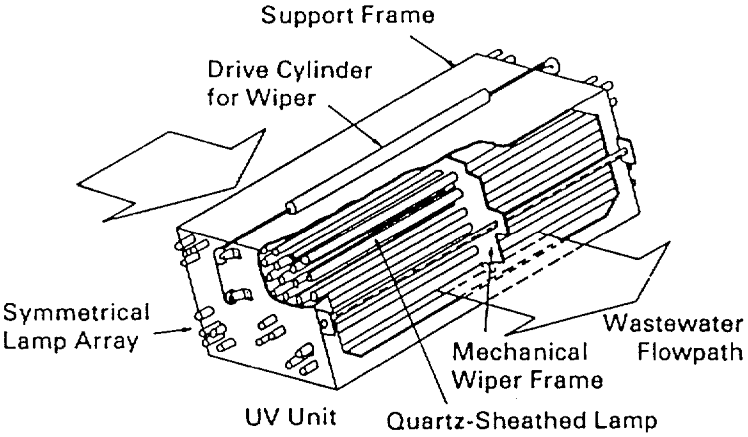
A number of configurations exist that describe the arrangement of lamps relative to the direction of the flow. Figure 4.1 illustrates the three main reactor types: the perpendicular to flow quartz unit; the parallel to flow quartz unit and the fluorocarbon unit which necessarily has a parallel flow. Ideally in a UV reactor, flow conditions should be such that mixing is maximised in the direction perpendicular to flow and minimised in the direction parallel to the flow (plug flow), so that each element of water receives the same overall average intensity of radiation.

Table 4.1: Characteristics of medium and low pressure mercury lamps (Hanovia)

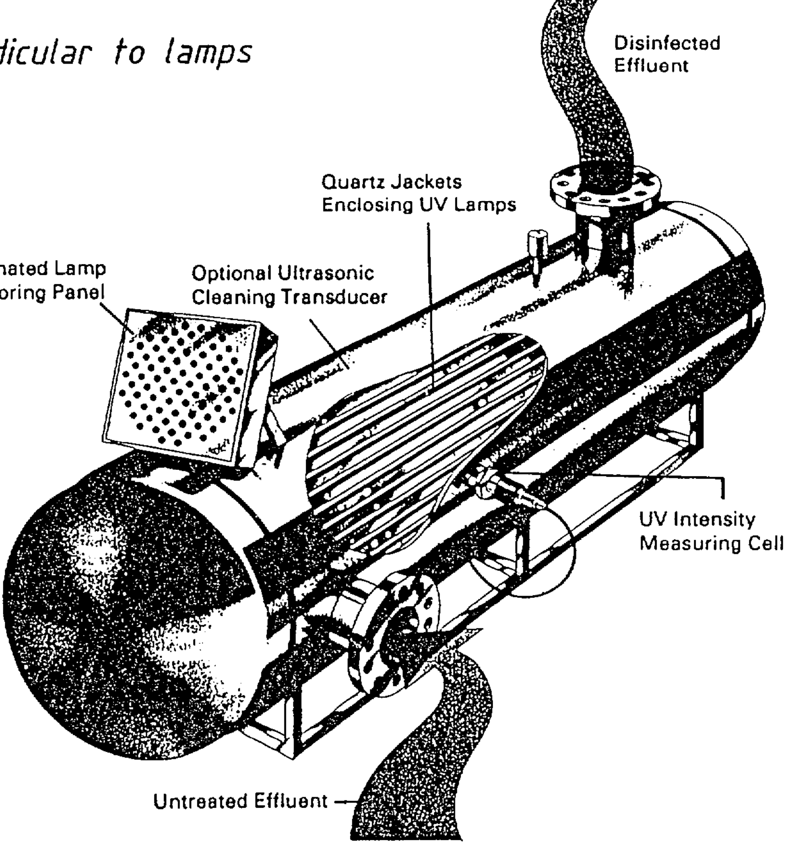
	Medium Pressure	Low Pressure
Pressure (atm)	1-3	0.01-1
Power rating (kW)	0.6-2.5	0.03
Effective output (Wm^{-2})	1720	67
Flow rate (m^3h^{-1})	up to 200	up to 1.5
Emission	Broad	254nm
Operating life (h)	1000-2000	5000-10000
Optimum temp	No	Yes (40°C)

Table 4.2: Theoretical UV lamp and flow rate relationships for medium and low pressure lamps at doses of 16 and 30 $mWscm^{-2}$ (Hanovia)

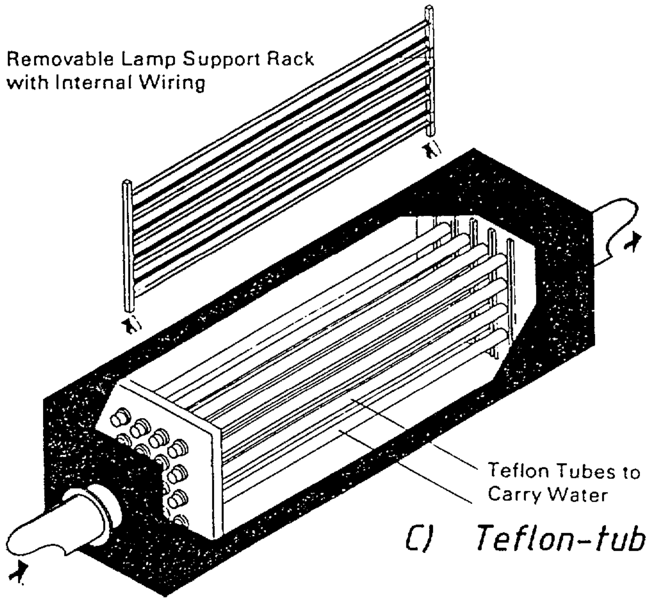
	Max flow rate at initial dose (m^3h^{-1})	
Single arc tube	16 $mWscm^{-2}$	30 $mWscm^{-2}$
30W low pressure	1.8	0.9
0.5kW medium pressure	22	12
1.5kW medium pressure	104	56



A) Quartz unit with flow perpendicular to lamps



B) Quartz unit with flow parallel to lamps



C) Teflon-tube unit

Fig 4.1 Typical reactor configurations for UV disinfection (EPA, 1986)

The polymer tube appears to achieve the nearest approximation to plug flow characteristics, whilst in both parallel and perpendicular flow quartz facilities, significant short circuiting can occur and some organisms pass with little exposure (Kreft *et al* 1986).

4.2.3 Flow rates

The flow rate is proportional to the number of lamps and thus there are no economies of scale. The typical UV output of a single low pressure mercury lamp in 67 Wm^{-2} measured at the wall of the quartz sleeve in the radiation chamber. As the flow rates increase, the output can be increased by using more lamps or a medium pressure lamp which has a higher output than a low pressure lamp. The flow rate capabilities of the two lamp types for pure water are given in Table 4.2. The flow rates for wastewater effluent will be lower than these due to the higher contact times required to achieve a similar dose. Operational wastewater disinfection plants, which typically use low pressure mercury lamps, indicate design flow rates ranging from 1 - 2.5 m^3h^{-1} per lamp for secondary effluent.

4.2.4 Cleaning

This is of prime consideration in UV disinfection of wastewater as fouling of the quartz or polymer sleeve can lead to decreased transmission and efficiency unless regularly cleaned.

In theory, fluorocarbon tubes should not be prone to internal fouling though in certain circumstances this may occur (Kreft *et al*, 1986). The polymer surfaces are degraded by cleaning and lose their ability to transmit UV light over time. Fouling of quartz sleeves can occur due to oil, grease, solids and inorganic scale on the wet side, and leakage of air and dust on the dry side of the quartz surface. Scaling is caused by inorganic salts of magnesium, calcium and manganese, which have lower solubilities at the higher temperatures found on the outer surface of the quartz sleeve. As well as routine cleaning, a complete overhaul of the reactor is recommended at least once a year, to clean all interior surfaces and determine the transmittance of the quartz/Teflon sleeves and lamp output. The quartz sleeve may be monitored for transmittance by removal of a representative fraction of the sleeve.

The quartz lamps may be washed with a mild soap solution, rinsed, and swabbed with alcohol, and the quartz sleeve interior surfaces cleaned using a gun-barrel type cleaning rod. The Teflon lamps should be cleaned in the same way and the tubes can also be swabbed with alcohol (EPA, 1986). Periodic chemical cleaning with a mild acid (oxalic or citric) and/or detergent is necessary for both the outer quartz or inner Teflon surfaces. For the quartz units, accessory equipment such as mechanical wipers and ultrasonic transducers have been employed whilst high pressure spray nozzles are used for both Teflon and quartz units.

Most of the quartz units in the US are equipped with mechanical wipers or ultrasonic equipment. At the Albert Lea facility in the US, (see Section 4.9), mechanical wipers in the form of a Teflon ring on a spring are used which are effective at reducing a build-up of scale and biological growth on the quartz surface. Ultrasonics are utilised at the Suffern, New York and Iowa installations but their efficacy is questionable, especially with hard water. High pressure nozzles may have some benefit in cleaning interior Teflon surfaces (EPA, 1986).

Cleaning frequency is determined by the effluent quality and may be necessary daily if chemical cleaning only is practised or once a week if a mechanical facility is employed. A specimen tube may be used to monitor for cleaning or alternatively *in situ* UV monitors may be used to measure UV intensity. However, these are also subject to fouling and should not be relied upon.

Frequent visual monitoring of the tubes is recommended and for this reason access to the tubes should be as simple as possible.
Cleaning problems at US plants has led to their abandonment in certain cases and would be a major hurdle in the successful operation of plants treating low quality effluent.

4.2.5 Safety

Since UV is generated on-site there are no dangers arising from transportation or storage, and hazards asssociated with it relate to the high electrical loads and exposure to UV radiation. Excessive exposure of personnel to UV should be avoided as it is known to cause sunburn, erythema and conjunctivitis, the skin and eyes being particularly vulnerable (WPFC, 1986). The American Medical Association have published exposure limits of 0.5 uWscm^{-2} for exposure at 254nm for up to 7h to prevent reddening of unprotected skin. Since average doses for wastewater are in the range 10,000 - 100,000 uWscm^{-2}, accidental exposure poses a human health risk (Hubly *et al*, 1985). Whilst a submerged lamp battery would be no hazard, it should not be operated while dewatered and dry. The Teflon units should have all covers in place during operation. Plastic shields protect against exposure but personnel should wear proper protective gear (WPCF, 1986).

4.3 **Mechanism of inactivation**

The UV region of the electromagnetic spectrum is generally defined as radiation of wavelengths between 40 and 400 nm, though the radiation reaching earth is normally in the range 287 - 390nm, the remainder having been filtered out by the atmosphere. The most effective biocidal effect occurs between the wavelengths 250 - 265nm, at which UV is absorbed by the nucleic acids RNA and DNA causing chemical alteration and the inability to replicate (EPA, 1986).

When UV is absorbed by genetic material, neighbouring base residues in the DNA or RNA (thymine and uracil respectively) dimerise, thus preventing pairing with a complementary base and interfering with replication. These dimers are the major cause of the lethal and mutagenic effects arising from UV (Wacker, 1963; Severin and Suidan, 1985; Venosa, 1983).

The dimerisation of neighbouring thymine residues in bacterial DNA was found to be more readily induced by UV radiation than uracil dimerisation. Uracil dimerisation occurs in viral RNA and this may explain the higher resistance of viruses to UV (Harris *et al*, 1987).

4.3.1 Photoreactivation

Though DNA synthesis is inhibited by even relatively small doses of UV, living organisms have evolved a defence mechanism to repair through photoreactivation (exposure to near UV at 340 - 360nm) or dark recovery repairs. However, intense UV irradiation produces so many lesions that the damage is irreversible.

Photoreactivation is caused by fission of the base dimers by a photoreactivating enzyme mechanism, or in the case of dark recovery, by two distinct enzyme systems. The phenonemon is more commonly associated with bacteria, as viruses lack the repair enzymes required (Harris *et al*, 1987). Organisms which have been shown to photorepair include *E.coli, Shigella micrococcus, Aerobactor* and *Penicilllium* whilst organisms which have no photorepair mechanism include *Haemophilus influenza, Streptococci, Diplococcus pneumoniae* and *Bacillus subtilis* (EPA, 1986). Reactivation is never complete and depends on the inventory of repair enzymes which differs between organisms (Chanda and Chatterjee, 1976).

The degree of recovery has major implications with regard to disinfection. One hour of sunlight is thought to increase the surviving fraction of microorganisms by a factor of 10 (Severin and Suidan, 1985).

4.4 Disinfection efficiency

The main factors governing the efficiency of disinfection by UV are the UV dose, which is a product of lamp intensity and contact time, and wastewater quality.

There have been many attempts to evaluate dosages for inactivation of a variety of organisms. However the difficulties inherent in measuring the UV dose, together with differences in the strain and physiological status of the test microorganisms, growth medium and stage of culture used, makes comparison between studies difficult. Nevertheless, comparisons within studies give a useful indication of the order of resistance of different organisms and of the magnitude of the dose required (see Table 4.3).

In a study designed to determine accurately the dose required to inactivate certain human pathogens, Chang *et al* (1985) found a similar order of resistance amongst bacteria, with viruses 3 - 4 times more resistant and bacterial spores and protozoan cysts up to 9 and 15 times more resistant than bacteria respectively (Table 4.3). These experiments, which were conducted on standard plate count microorganisms from secondary effluent as well as a variety of cultured bacteria, viruses and protozoan cysts, found a tendency for wastewater coliform cells to be protected by association with larger particles, with the effect highlighted at low levels of survival. The results for the cultured organisms should therefore be considered as baseline UV dosages for inactivation.

Conditions encountered in practice, where indigenous pathogens are shielded from the UV, require higher dosages. Wastewater UV disinfection requires higher doses still than those practised in potable water disinfection. Typical dosages for secondary effluents at operational UV plants in the US range from 30 - 50 mWscm^{-2} (White *et al*, 1986) which in comparison to values in Table 4.3 would suggest that this is insufficient for complete inactivation of certain viruses, protozoan cysts and bacterial spores.

Table 4.3. UV doses required for inactivation of various microorganisms

	Dose to achieve % inactivation ($mWscm^{-2}$)		
	100% (Jevons,1982)	99.9% (Chang,1985)	90% (Hanovia,1987)
BACTERIA			
E. coli	6.6	7	3.0
Pseudomonas aeruginosa	10.5		5.5
Salmonella	10.0		
Salmonella typhimurium	15.2	7	2.14
Salmonella enteritidis	7.6		4.0
Streptococcus lactis	8.8		6.15
Streptococcus viridans	3.8		2.0
Streptococcus faecalis		10	4.5
Staphylococcus aureus	6.6	7	2.18
Legionella pneumophila			2.04
Shigella sonnei		7	
VIRUSES			30-40
Bacteriophage (*E. coli*)	6.6		
Influenza	6.6		3.4
Tobacco mosaic	440		240
Rotavirus		25	
Poliovirus		25	
PROTOZOA			
Nematode eggs	92		
A castellanii cysts		105	
SPORES			
Bacillus subtilis	22	60	11.6*
Bacillus megaterium	5.2		2.73*

* Data from Ohren & Wiik (1986)

A two year pilot scale study at Port Richmond, New York demonstrated the application of UV disinfection to treated wastewater. Two quartz units (differing only in the spacing between the quartz surface) and a Teflon unit were used to treat secondary effluent and high-rate settled raw wastewater. In the secondary effluent, a 3-4 log reduction in coliforms was achieved whilst up to 3 log reductions were achieved in the primary effluent. The project at Port Richmond led to the development of a protocol for the design of a UV disinfection process (EPA, 1986).

In laboratory scale studies on the UV disinfection of secondary effluents, Oliver and Cosgrove (1975) demonstrated that 2-3 log reductions in total and faecal coliforms and faecal streptococci may be achieved with relatively low dosages. The effluents were of good quality (suspended solids 9-21 mgl^{-1} and turbidity 2.5-5.5 FTU). To demonstrate the effects of size distribution of suspended solids in effluent, samples of raw sewage (suspended solids $\approx$ 150 mgl^{-1}) subjected to the same dose were shown to achieve a maximum of only 1 log reduction. Ultrasonication appeared to disperse the particulate aggregates making the sample more susceptible to UV treatment.

The work that has been conducted on the inactivation of pathogens in low quality wastewaters indicates that significantly higher doses of UV are required to achieve similar reductions as in potable water disinfection. In pilot studies conducted by Zukovs *et al* (1986) on combined sewer overflows (CSO), a relatively high dosage of 356 mWs cm^{-2} achieved reductions of greater than 3 logs for faecal coliforms, enterococci, *Pseudomonas aeruginosa* and greater than a 1 log reduction in salmonellae. Following photoreactivation the overall reductions were slightly lower but 2-3 log reductions could still be attained (see Section 4.7.1).

Comparison of the efficency of UV with that of chemical disinfectants is not strictly valid. Nevertheless the range of doses for the inactivation of different types of pathogens appears narrower than that for chlorine (Chang *et al*, 1985). Comparative data for chlorine aand UV inactivation are given in Table 4.4. Studies on chlorine disinfection have found that in comparison to *E.coli*, viruses required up to 40 times the dose of free chlorine (Scarpino *et al*, 1974) whilst bacterial spores were 400 times more resistant (Morris, 1975).

In a study conducted on secondary effluent by Whitby *et al*, (1984), the inactivation of various pathogens using UV and chlorine was investigated and the degree of photoreactivation was also assessed (Table 4.5). A UV dosage of 36.8 mWs m^{-3} of effluent achieved 4 log reductions in total coliforms, faecal coliforms, faecal streptococci and 2-3 log reductions in *Pseudomonas aeruginosa* and bacteriophage. The spore forming bacterium *Clostridium perfringens* was more resistant and a 1.8 log reduction was achieved at a higher dosage of 82.8 mWs m^{-3} of effluent.

Indicator bacteria levels in the chlorinated effluent were similar to levels found in the UV effluent following photoreactivation; with the notable exception of *C. perfringens*, which was destroyed more effectively by UV. UV is also more effective at destroying bacteriophages which suggests it may have better virucidal properties than chlorine. Photoreactivation led to an increase in coliforms of 1 log at maximum. Regrowth from chlorinated effluent did not appear to be a problem.

The results of these and other experiments would suggest a lower minimum dose for the complete inactivation of all pathogens is required for UV compared to chlorine; and the use of indicator organisms underestimates the efficiency of UV at the expense of chlorine.

The lethal dose values determined from cultured pathogens give the minimium UV dose necessary for inactivation but are not representative of conditions encountered in practice, where pathogens are shielded from the UV. Studies on the survival of

Table 4.4: Relative doses of UV and chlorine required to achieve equivalent microorganism reductions

Microorganism	UV (Chang *et al*,1985)	chlorine (Morris,1975; Scarpino *et al*,1974)
Bacteria	1	1
Viruses	3-4	40
Bacterial spores	9	400
Protozoan cysts	15	-

Table 4.5: Log reduction of various pathogens by UV and chlorine in secondary effluent and mean value following photoreactivation (UV only) (Whitby *et al*, 1984).

	UV (36.8 mWs m^{-3})			Cl_2 (0.4 mgl^{-1} resid)	
	geometric mean $100ml^{-1}$			geometric mean $100ml^{-1}$	
	Influent	Effluent	Photoreactivation	Influent	Effluent
Total coliform	53030	4 (4.1)	66 (2.9)	40827	101 (2.6)
faecal coliform	15645	0.3 (4.7)	14 (3.0)	7203	0.4 (4.3)
faecal streptococci	1239	0.04 (4.5)	0.2 (3.8)	578	14 (1.6)
Clostridium perfringens	1854	358 (0.7)	323 (0.8)	1683	1292 (0.1)
P.aeruginosa	151	1 (2.2)	1.1 (2.1)	153	1.4 (2.0)
Bacteriophage	3530	0.95 (3.6)	-	6233	304 (1.3)

Figures in parentheses represent log reductions.

pathogens for different UV doses have been made for specific effluent qualities (Qualls *et al*, 1983). Further research is needed to evaluate UV dosages in relation to the survival of pathogens for a representative range of wastewater effluent qualities.

4.4.1 Photoreactivation

The influence of photoreactivation on the sensitivity of selected microorganisms was investigated by Harris *et al* (1987).

Experiments conducted on cultured cells showed that following photoreactivation, the sensitivities of *E.coli* and *Streptococcus faecalis* were not significantly different but differed considerably from that of the UV inactivated bacteria. A 2-3 log photoreactivation of the bacteria occurred which was in contrast to the findings by Whitby *et al* (1984) of a maximum 1 log increase of coliforms. Without photoreactivation the viruses require 6-10 times the dose for *E.coli* and 3-6 times the dose for *S.faecalis* for a 3 log reduction, which is in agreement with the findings of Chang *et al* (1985). Following photoreactivation, the dose required for bacteria approximately doubles but is stilll much lower than that required for viral inactivation. The results on the inactivation of reovirus and poliovirus showed the higher sensitivity of the poliovirus which was thought to be due to the fact that poliovirus has a single protein coat and is three times smaller than reovirus; the larger surface:volume ratio making it a better target per unit biomass for UV radiation.

4.5 **Factors affecting efficiency**

The two main factors limiting UV efficiency are the dose and the wastewater quality. This may be described in terms of a mathematical model (Scheible, 1987):

$$N = N_o \exp(-kIt) + Np$$

where:

N_o = initial density microorganisms (organisms $100ml^{-1}$)

N = density after UV (organisms $100ml^{-1}$)

I = intensity of UV ($uWcm^{-2}$)

t = time(seconds)

k = constant($cm^2\ uWs^{-1}$)

Np = bacterial density associated with particulates (organisms $100ml^{-1}$)

The dose (intensity x time) is governed by process parameters whilst the wastewater quality is governed by pretreatment, though the two are not wholly independent. For example the intensity of light transmitted is governed by Lambert's Law which depends on the absorbance and pathlength of the water.

4.5.1 UV dose

The intensity, or rate at which energy is delivered to the wastewater, tends to be calculated at the rated output of the lamp, but average intensity must be adjusted for ageing and the reduction of output as UV passes through the respective media separating the source from the wastewater (quartz or non-reactive polymer) as well as any coating or film that develops on the surface of these media. The UV dose is commonly expressed as mWs cm^{-2}.

4.5.2 Water Quality

Ideally the wastewater to be treated will readily transmit UV, have a low initial density of coliforms and a low solids content. All operational plants in the US and Canada have some form of wastewater treatment prior to disinfection. Pilot studies on lower quality wastewaters (Oliver and Cosgrove 1975; Zukovs *et al*, 1986; Hanovia, 1987) suggest that there is a threshold effluent quality above which UV treatment is feasible both practically and economically. The parameters of water quality exerting the greatest influence on UV efficiency are concentrations of suspended solids, and to a lesser extent, ionic salts.

The high levels of suspended solids in wastewater effluents exert a two-fold effect on efficiency. They absorb and scatter the light (Qualls *et al*, 1983) but more importantly they harbour bacteria which are then partially protected from the UV rays. The survival of coliforms in wastewater is directly related to the number and size of particles, although for practical purposes a surrogate parameter such as solids concentration is more easily measured. Thus larger aggregates of suspended solids have a greater limiting effect than very small particulates as measured by turbidity. In secondary effluent most of the large aggregates have been removed but it is unlikely that adequate disinfection could be achieved in raw sewage, regardless of UV dose (Oliver and Cosgrove, 1975).

To achieve 1000 total coliforms 100 ml^{-1} in UV irradiated effluent, it was estimated that a UV dose of 26 $mWscm^{-2}$ would be required for an effluent with a suspended solids concentration of < 20 mgl^{-1}, and a dose of 42 $mWscm^{-2}$ for suspended solids >20 mgl^{-1} (Qualls *et al*, 1985). Filtration prior to UV treatment has been found to be effective due to the removal of particulate-protected organisms rather than an increase in UV intensity in the less turbid solutions (Johnson and Qualls, 1981). One further effect of high solids concentrations in wastewater is that clumping of organisms distorts the results from the plate count method which is used to enumerate viability. This method fails to discriminate between the colony formed from a single organism or a clump of organisms (Galassop and Sharp, 1965).

Other water quality parameters which adversely affect the efficiency of UV disinfection are levels of iron and manganese though this is of more importance in potable water treatment and unlikely to have significant impact in wastewater disinfection.

4.6 Toxicity and by-product formation

UV is a physical rather than a chemical disinfectant therefore it is unlikely to produce any by-products nor is it possible to overdose. The converse of this is that it does not provide a lasting disinfection residual, but this is of more concern in potable water treatment than when disinfecting prior to marine discharge.

In a study to investigate the effects of disinfection on nonvolatile organic constituents and the formation of micropollutants Jolley *et al* (1982) found that UV irradiation at disinfectant levels produced only slight chemical changes in the non-volatile organic constituents. Only at dosages higher than normally used for disinfection were any pronounced chemical effects observed. Whilst disinfection with chlorine or ozone led to an increase in the the mutagenicity of some constituents in concentrates of several wastewater effluents, the evidence for increased mutagenicity in UV-irradiated effluent was not clear. Although in one case, UV produced some non-volatile mutagenic components it was not posible to detect the mutagenicity in the separate fractions, which may have been destroyed in the subsequent chromatographic separations.

UV irradiated effluent exhibits no toxicity to fish; being shown to be non-lethal after 48 h exposure to rainbow trout (*Salmo gairdnerii*) yearlings. In comparison, an evaluation for chlorine produced 50% mortality in 7 h and 100% mortality in 24 h (Whitby *et al*, 1984).

4.7 Pilot studies

Though all full scale UV disinfection is presently conducted on secondary effluents, pilot studies in the US and UK have investigated the efficiency on wastewaters of lower optical and microbiological qualities (Zukovs *et al*, 1986; Hanovia, 1987).

The studies by Zukovs *et al* (1986) were conducted on combined sewer overflows (CSO) (equivalent to a medium strength wastewater with lower than normal ammonia levels) whilst trials in the UK, conducted by Hanovia Ltd in conjunction with a water authority, investigated UV disinfection for primary settled sewage and biofilter effluent.

4.7.1 Zukovs *et al* (1986)

An experimental study by Zukovs *et al* (1986) addressed the technical and economic feasibility of using UV irradiation for the disinfection of low quality wastewaters. The disinfectant efficacy of UV was assessed and compared to that of chlorination. The characteristics of the simulated CSO are shown in Table 4.6. The efficiency of the UV reactor at various UV dosages (126 - 315 $mWscm^{-2}$ average) was first evaluated by the log reduction of faecal coliforms, enterococci, *Pseudomonas aeruginosa* and *Salmonella* spp. A target 4 log inactivation of faecal coliforms was then used to select a dosage for a steady state run. Eight quartz low pressure UV lamps with a parallel-to-flow configuration were used, with a rated output of 8-14 W $lamp^{-1}$. Matching the target dosages to the actual dosages proved difficult because of the variable character of the CSO.

The results of the steady state run are shown in Table 4.7. The geometric mean dosage was 356 mWs cm^{-2}, which was higher than the target dosage of 325 mWs cm^{-2}, and mean reductions in faecal coliforms, enterococcus and *P. aeruginosa* were 3.2, 3.3 and 3.0 logs respectively. A mean reduction in *Salmonella* spp. of 1.5 logs was also observed. Investigation of photoreactivation showed that whilst reductions were lower when this was taken into account, it did not have a statistically significant effect. The analogous results with chlorine, in which a 25.5 mgl^{-1} total chlorine residual was used as the control parameter at a 2 min contact time, showed that greater than 4 log reductions in the indicator organisms were achieved and *P.aeruginosa* and *Salmonella* were reduced by 3 and 1 log respectively.

Table 4.6: Characteristics of simulated CSO wastewater (Zukovs *et al*, 1986)

Suspended solids (mgl^{-1})	Average transmission (%)	BOD (mgl^{-1})	NH_3-N (mgl^{-1})	Faecal coliforms ($100ml^{-1}$)
181 (total) 146 (volatile)	2.8	176	12.3	10^6

Table 4.7: Log reduction of bacteria in steady state run of UV disinfection of combined stormwater overflow (CSO) (Zukovs *et al*, 1986)

	Dose ($mWscm^{-2}$)	Influent ($100ml^{-1}$)	Effluent ($100ml^{-1}$)	Log reduction	Log reduction after PR*
Faecal coliform	297 - 416	$4.3x10^6$	3100	3.14	2.87
Enterococci		$3.5x10^6$	1800	3.29	3.04
P. aeruginosa		10,700	<10	3.03	2.85
Salmonella		15	<0.5	1.48	1.33

* photoreactivation

The conclusions drawn from the study were that whilst reductions of greater than 3 logs could be achieved for indicator and pathogenic organisms, the dosages and contact times required for the low quality CSO wastewater were considerably greater than those used in practice on secondary effluents. Since UV dose is directly proportional to costs, this would put severe financial limitations on UV disinfection of effluent of comparable quality to CSO. This is verified by their comparisons of estimated costs for UV versus chlorination/dechlorination for plants treating up to 50,000 m^3d^{-1}. Though operating costs are of the same order of magnitude, the capital costs are significantly higher (see Section 4.9.1).

4.7.2 Ladock and Par (Hanovia/South West Water)

In 1987, South West Water and Hanovia Ltd conducted trials to determine the efficacy of UV in the inactivation of coliforms in primary settled sewage and biofilter effluent. The trials were conducted on two primary settled sewages from Ladock and Par sewage treatment works in Cornwall. In addition, the effect of increased UV transmission in a percolating filter effluent was assessed.

The characteristics of the wastewaters investigated are given in Table 4.8. The efficiency of inactivation was determined for each effluent at various dosages by altering the flow rate.

The maximum flow rate to achieve a certain kill (to ensure compliance with EEC directive limits assuming a 100-fold dilution at outfall) was then determined. The UV facilities and dosages used in the trial are shown in Table 4.9. The results of the trial (Table 4.10) showed that bacterial reductions of 1 - 2 logs could be achieved on a regular basis. However, less than a 2 log reduction would fail to conform to the EEC standard of 10^4 total coliforms 100 ml^{-1}, therefore only at the lower flow rates was the required kill achieved.

Table 4.8: Characteristics of sewage effluents used in trials on primary effluent and biofilter effluent (Hanovia/SWW, 1987)

Wastewater	SS (mgl^{-1})	Average Transmission (%)	Total coliform ($100\ ml^{-1}$)	Faecal coliform ($100\ ml^{-1}$)
Primary (Ladock)	67-96	2-4	10^8	10^7
Primary (Par)	135-139	3	10^8	10^7
Biofilter	26-55	16-28	10^7	10^6

Table 4.9: UV facilities and dosages used in trials on primary effluent and biofilter effluent (Hanovia and SWW, 1987)

Type	Config	No of lamps	Rated output ($Wlamp^{-1}$)	Design flow rate (m^3h^{-1})	Target dose ($mWscm^{-2}$)	Average dose ($mWscm^{-2}$)
Quartz medium pressure	parallel	1	500	5(max)	43(max) 0.5-4.2 (ave)	3-45

Table 4.10: Percentage reductions in coliform bacteria in trials on primary and biofilter effluent (Hanovia/SWW, 1987)

	Dose ($mwscm^{-2}$)	Influent ($100ml^{-1}$)	Reduction (%)	Flow rate for required kill (m^3h^{-1})
Primary(Ladock)				
Total coliform	3-13	1×10^8	85.3-99.3	
E.coli		1×10^7	79.5-99.3	0.5
Primary(Par)				
Total coliform	10-19	7×10^8	99.3-99.8	
E.coli		8×10^7	98.93-99.6	<0.5
Biofilter				
Total coliform	16 - 45	2×10^7	81.36-97.05	
E.coli		4×10^6	79.25-95.8	1.7

Table 4.11: UV capacity calculated for maximum flow of 500 m^3h^{-1} primary effluent extrapolated from pilot trials (Hanovia/SWW, 1987)

	Pilot	Extrapolated full scale (max flow)	(ave flow)
Size of lamp (kW)	1 x 0.5	28 x 2.5	12 x 2.5
maximum flow (m^3h^{-1})	<0.55	500	180

UV disinfection was shown to be dependent on both the flow rate and the suspended solids content of sewage with better kill rates achieved as the solids content decreased. The variation in raw sewage strength and flow made it difficult to predict a kill for a given dose and necessitated frequent monitoring of influent and effluent bacterial levels.

The coliform reductions for the biofilter effluent were lower than for the primary effluent, which was unexpected considering the improved transmission and bacterial quality of the biofilter effluent. This may have been due to the fact that a higher proportion of bacteria have an attached growth habit in biofilters, being adsorbed onto particulate matter following percolation, and thus are less susceptible to UV disinfection. This indicated that coliform kills cannot be predicted on the basis of suspended solids and percentage transmission alone, but that the degree of clumping must also be taken into account.

The UV equipment used was found to be reliable though daily cleaning of the quartz sleeve was necessary, leading to recommendations for an automated mechanism.

Conclusions drawn by South West Water were that UV could achieve compliance with the EEC standard for coliforms following marine discharge of settled sewage but that an automatic cleaning mechanism would be necessary fo the quartz tube. It was emphasised that no viral enumerations had been undertaken. Since viruses tend to be solids-associated and therefore less likely than coliforms to be killed by UV, it was observed that receiving waters may still fail to comply with the EEC standard on the basis of viruses.

4.8 Full scale operation

Ultra-violet disinfection was not considered a serious rival to chlorination in the US until the mid 1970s when viable alternatives were being sought. Whilst it was viewed as a promising technique, disadvantages included lack of information on application to low quality wastewater, lack of design protocol and the past history of fouling (EPA, 1986). Fourteen full scale plants were subsequently installed, funded by the USEPA under their 'Innovative and Alternative Technology' funding, which provided much information on which to base future design modifications. In 1986, a total of 53 UV wastewater installations were operational in North America; a summary of UV installations which were operational, or in the design or construction phase, in 1986 is shown in Table 4.12.

The operational UV installations in the US and Canada were evaluated in an EPA project in 1984, which selected 6 for site visits on the basis that they were representative of the UV facilities available (White *et al*. Flow rates at the 6 sites ranged from 0.013 m^3s^{-1} (876 m^3d^{-1}) to 0.175 m^3s^{-1} (15120 m^3d^{-1}) and all had primary and secondary pretreatment prior to disinfection. The UV units were of 3 types: polymer fluorocarbon tubes or quartz sleeves of parallel and perpendicular flow.

The difficulties of comparing dosage between facilities with the variety of configurations and number of lamps was overcome by using an exposure factor calculated by dividing the total lamp output wattage by the design flow rate for that unit. This was based on an output rating of 26.7W of UV light per lamp. This differs from the dosage of UV, which is calculated in units of $mWscm^{-2}$.

$$\underset{(Wsl^{-1})}{\text{Exposure factor}} = \frac{\text{Total lamp output wattage (W)}}{\text{Design flow rate } (ls^{-1})}$$

Characteristics of one UV facility, typical of those studied, are shown in Table 4.13. This plant was put into operation in November 1981 and operates on high quality secondary effluent, with a discharge design of 200 faecal coliforms 100 ml^{-1} over a 30 d average.

Table 4.12: UV wastewater installations in US and Canada,1986 (EPA,1986)

Design flow rate (m^3d^{-1})	In operation	In construction	In design
<380	15	7	-
380-1900	17	10	10
1900-3800	7	5	4
3800-19000	11	14	11
19000-38000	-	-	-
38000-190000	1	-	2
>190000	-	1	-
Total	53	30	34

Table 4.13: Characteristics of one UV facility typical of those monitored in the 1984 EPA study (White *et al*, 1986)

Type	Lamp no.	Lamp output (W)	Design peak (m^3s^{-1})	Flow rate average (m^3s^{-1})	Current average (m^3s^{-1})	UV exposure (wsl^{-1})
Quartz perpendicular	392	26.7	0.175	0.10	0.04 - 0.12	29.8

4.8.1 Plant performance

Faecal coliform effluent levels for the plant detailed in Table 4.13 were well within the discharge limit for a 7 month monitoring period reported in 1983. However insufficient data was available to evaluate disinfection performance at the other sites since the necessary microbiological data was not always collated on a frequent basis, nor were influent faecal coliform numbers measured routinely.

The limited data that were available indicated that the remaining plants were are all operating within discharge levels of 1000 faecal coliforms 100 ml^{-1} and three were discharging less than 200 faecal coliforms 100 ml^{-1}. All six sites were operating on high quality secondary effluent with suspended solids concentrations and flow rates below design levels and consequently were discharging effluents with suspended solids concentration lower than required by permit.

4.8.2 Operational difficulties

The following operational difficulties were reported:

a) Electrical problems were frequently encountered during start up and initial operation, which were largely caused by inadequate ventilation leading to overheating. The complexity of the electrical system also hindered ease of maintenance.

b) Mechanical and hydraulic problems were also experienced, unrelated to the UV process itself, and resulted in design modifications.

c) Automatic controls of UV output, to conserve power during low flow rates, caused problems at 4 out of 5 plants, leading to a reversion to manual control.

d) Cleaning: two of the quartz units used ultrasonic transducers and two used mechanical wipers, all four supplemented by chemical cleaning. However the use of mechanical cleaning equipment did not allow determination of how effectively the units were being cleaned. The UV intensity meters were not sensitive enough to detect differences in intensity before and after the transducer had been used.

Internal UV sensors were subject to the same fouling as quartz and tube units and should not be relied on for control, although they are useful to signal the loss of all UV transmittance from a bank of lights.

These observations led to a number of recommendations to design engineers; the most important of which stressed the need for pilot testing to establish design criteria. Mechanical problems that required further development were identified as:

a) improvements in lamp and sleeve cleaning mechanisms
b) methods of online control of UV dose application (to conserve power consumption when performance is adequate)
c) methods for predicting effluent quality.

4.8.3 Reported costs

Capital costs for the systems on a 1984 price basis ranged from just over \$12,000 for a 2.5 kW system to almost \$300,000 for a 25 kW unit. At a current exchange rate of \$1.00 = £0.57, this represents a cost of £6,840 - 171,000.

Costs for housing the systems varied greatly. Five out of the six installations housed the UV system inside but floor space was not always proportional to the system size. Operation and maintenance costs included manhours for routine maintenance and analytical work; replacement parts and supplies; power consumption and cleaning chemicals. Operational costs were unavailable at the time of the study. Maintenance requirements were estimated at 8 manhours per week for the smaller facilities (<100 lamps) and 12 manhours per week for the larger plants (>200 lamps).

4.9 Costs

Reported cost of different UV facilities are not strictly comparable due to assumptions concerning wastewater quality, discharge requirements, amortisation periods and interest rates, prices of electricity, civil engineering inclusions and currency rates.

More useful comparisons are obtained when UV costs have been directly compared to an alternative disinfection process, such as ozone or chlorine, which give an indication of relative costs. However, these costs will be specific for a particular wastewater quality and discharge requirement; a particularly important point in that discharge requirements tend to be more stringent in the US and France where many of these costs have been derived. A significantly higher effluent quality in terms of suspended solids and COD will require higher UV dosages and hence costs, but may not be necessary for disinfection prior to marine discharge.

The costs for UV processes include the following components:

Capital

UV lamps
Installation
Ballasts
Control instrumentation
Cleaning equipment

A basic space requirement for a single module UV system was estimated at 10m^2 increasing to 25m^2 for larger modules (EPA, 1986). Thus a 500 kW system (6000 lamps in 10 modules) would require 250 m^2. The power supplies and instrumentation require weatherproof protection, otherwise the system can be housed in a standard building.

Operation and Maintenance

UV is a capital intensive process with equipment requirements directly proportional to design peak hydraulic and performance needs.

Material replacement

Lamps, ballasts quartz/teflon units

Power consumption

Ancillary power is minimal. Total power per lamp for a 1.5m arc lamp is typically 80W including ballasts (EPA, 1986).

Cleaning chemicals

Labour

a) Direct O&M tasks: 2-3hWk^{-1} (<100 lamps)
15-30hWk^{-1} (>1500 lamps)
b) General maintenance: (half of above)
c) System overhaul: 16h per 100 lamps
Total: 120 lamps, 10kW system: 40 man-days y^{-1}
5000 lamps, 400 kW system: 400 man-days y^{-1}

A cost curve for various sizes of UV facilities was estimated by Schieble (White *et al*, 1986) which was constructed from bid prices by UV manufacturers in the US (1984 $) (Figure 4.4). Capital costs at the operational sites visited in the EPA study (see Section 4.8) found 5 out of 6 plants exceeded the predicted values, due to development costs. None of the facilities had been in operation long enough to obtain operation and maintenance costs, which largely arise from replacement part costs; nor were power costs for the UV process alone available.

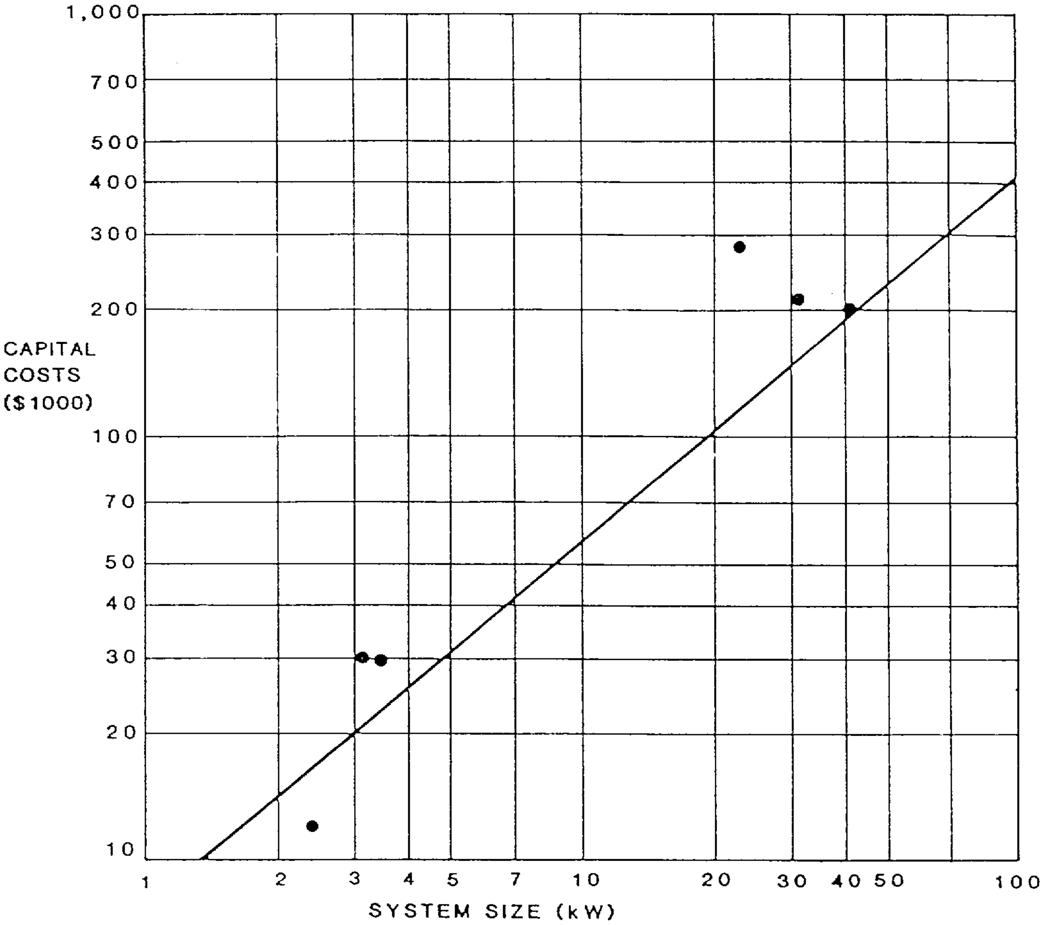


Figure 4.4 Capital costs for UV equipment at 6 sites visited in an EPA study (•) compared to previous EPA derived cost curve (White et al, 1986)

As a result of pilot trials on primary settled sewage (Section 4.7.2), Hanovia estimated costs for a unit treating up to 12,000 m^3d^{-1}. Hanovia estimated that treatment of primary effluent on a large scale with a maximum flow of $500m^3h^{-1}$ would require 28 2.5 kW units (Table 4.14). At an average operating cost of 158 ph^{-1} ($369ph^{-1}$: max flow) this would give daily operating costs of £38. The importance of pilot testing was stressed for confirmation of the size of facility required for a given flow rate and sewage composition.

One of the largest UV plants in the US is Albert Lea, Minnesota, which was designed for a flow of 47,300 m^3d^{-1}. The effluent quality limits are extremely stringent due to the ecological sensitivity of the receiving river and disinfection is the final stage in a process involving primary, secondary and tertiary treatment. The entire project including access works was constructed in 1983 for $34 million (approximately £19.4 million). The UV system comprised 4 separate units of 324 lamps; each capable of treating 250 ls^{-1} effluent. The costs are shown in table 4.15 (Kirkwold, 1984).

4.9.1 Cost comparison for UV versus chlorination/dechlorination

The costs of UV disinfection compared to the chlorination/dechlorination process as applied to combined sewer overflow were estimated by Zukovs *et al* (1986) in Canadian dollars (amortised over 20 y at 7% discount rate) for flow rates of 5000-500,000 m^3d^{-1}. The costs on a 1985 price basis are shown in Table 4.16.

Capital costs included allowances for excavation, screening, flow metering, grating cover, service building; the cost of open channel and UV lamps and of chemical storage tanks, pumps and associated piping. Operation and maintenance costs covered allowances for power consumption; labour; replacement of UV lamps; and chemical consumption.

Table 4.14: Capital and operating costs for UV disinfection based on pilot trials with primary and biofilter effluent (Hanovia/SWW, 1987)

		Max flow rate 12,000 m^3d^{-1}	Ave flow rate 4,320 m^3d^{-1}
No of 2.5kW units		28	12
Capital			
Units (£)		250,000	-
Chemical cleaning system (£)		10,000	
Operation & Maintenance			
(at 5.27pkWh^{-1})			
power	ph^{-1}	369	158
	pm^{-3}	0.74	0.88
Lamp replacement after 3000h (£)		135	

Table 4.15: Operational costs for a UV disinfection plant treating an average flow of 20,300 m^3d^{-1} (Kirkwold, 1984)

	operating cost (¢m^{-3})
Power (5¢kWh^{-1})	0.12
Lamp ($70; 7500h)	0.37
Labour (0.5h $lamp^{-1}$)	0.04
Total(¢m^{-3})	0.53
(pm^{-3})*	0.3

* conversion of 1984 US$ value at 1988 exchange rate of 1 US$ = £0.57

Table 4.16: Comparison of capital and operating costs for UV and chlorination/dechlorination disinfection for a range of plant sizes (Zukovs *et al*, 1986)

Flow rate	UV		chlorination/dechlorination	
(m^{3}d^{-1})	Capital	Operation & Maintenance	Capital	Operation & Maintenance
5,000 ($)	245,200	18,110	50,560	16,790
*(£)	110,000	8,000	23,000	8,000
50,000 ($)	2,208,108	78,925	84,120	60,700
(£)	993,500	35,500	38,000	27,000
500,000 ($)	21,801,000	672,700	380,305	496,000
(£)	9,810,500	303,000	171,000	223,000

*Conversion of 1985 Canadian dollar value at 1988 exchange rate of 1 Canadian $ = £0.45

Table 4.17: comparison of costs of UV, ozone and sequential ozone/UV disinfection for a range of plant sizes (Venosa *et al*, 1984)

Flow rate (m^3d^{-1})		UV	O_3	O_3/UV
Capital				
3,800	$	82,000	300,000	
	£*	47,000	171,000	
38,000	$	660,000	1,700,000	
	£	376,000	969,000	
950,000	$	1,660,000	3,300,000	
	£	946,000	1,881,000	
Total				
3,800	$\$m^{-3}$	0.032	0.074	0.041
	£m^{-3}	0.018	0.042	0.023
38,000	$\$m^{-3}$	0.029	0.045	0.024
	£m^{-3}	0.017	0.026	0.014
950,000	$\$m^{-3}$	0.029	0.038	0.022
	£m^{-3}	0.017	0.022	0.013

* Conversion of 1984 US dollar value at 1988 exchange rate of 1US$=£0.57

Operation and maintenance costs were estimated assuming:
Labour = $11.80/h (£6.70/h)
power = $0.042/kwh (0.024/kwh)
UV lamp = $40 (£23)

No of UV lamps (26.7W output) for 3 log reduction:
= 169 for 3,800 $m^{-3}d^{-1}$
= 1690 for 38,000 $m^{-3}d^{-1}$
= 4225 for 950,000 $m^{-3}d^{-1}$

There was no indication of the discharge requirements on which the costs were based, although pilot testing had involved relatively high dosages for UV and chlorine to achieve the target 4 log reduction of fecal coliforms. At all flow rates, capital costs for UV were higher than the chlorination system, which showed distinct economy of scale. Operation and maintenance costs were of a comparable magnitude.

4.9.2 Cost comparison for UV versus ozone

A study investigating the possible synergistic effects of an ozone/UV system compiled cost data from manufacturers for the separate and combined systems (Venosa *et al*, 1984). The estimates were based on a domestic secondary effluent with a target of 3 log reduction of faecal coliforms and flow rates of between 3,800 m^3d^{-1} - 950,000 m^3d^{-1}.

Capital costs (including M and E and supervision) and total costs (with capital amortisation at 7% over 20y) are given in Table 4.17. For a small plant, UV appeared to be the cheaper option at 1.8 pm^{-3} but at a larger scale, the combination of ozone followed by UV gave a total cost of 1.3 pm^{-3} as opposed to 1.7 pm^{-3} and 2.2 pm^{-3} for the individual processes respectively.

4.10. Conclusions

1. UV is an effective disinfectant for a range of microorganisms. Although certain bacteria can photorepair, this does not significantly reduce the overall inactivation efficiency. It is a more effective virucide than chlorine, requiring a much lower dose in comparison to that for bacterial inactivation.

2. UV is technically feasible for large scale wastewater disinfection given that the wastewaster is of a sufficiently high quality, with characteristics amenable to UV disinfection. There are currently 53 wastewater plants in the US using UV for disinfection of secondary effluents. The main problems experienced have been due

to fouling and electrical faults, but continued refinement of design and performance parameters should eliminate these in future installations.

3. There are insufficient operating data to predict the performance of UV for lower quality wastewaters. Pilot studies suggest that inactivation efficiency is limited by high suspended solids concentrations.

4. UV is one of the most benign disinfectant processes in terms of operating safety and environmental effects. There are no direct toxic effects and little evidence to suggest that harmful by-products are formed.

5. After chlorination, UV is one of the most economical processes available for treatment of treated effluents. The cost of the UV generator itself is relatively low, but costs of any necessary pretreatment would add substantially to the capital costs involved in treating raw sewage. The main operating and maintenance costs are replacement of the lamps and power consumption.

5. CLARIFLOW

5.1 Introduction

Clariflow is a physico-chemical treatment method which utilises the efficiency of lime as a disinfectant and coagulant. It was developed recently in the UK by Blue Circle in conjunction with Southern Water and Portsmouth Polytechnic, as a single stage process for pretreating screened sewage prior to coastal discharge. It has been operational at Sandown, Isle of Wight, since 1985, where four clariflow units served by two flocculation tanks are capable of treating up to 21,000m^3d^{-1} of raw screened sewage.

5.2 Production and application

A lime based chemical slurry with the trade name of Clarifloc is produced by Blue Circle Industries plc. Clarifloc contains lime, a weighting agent and polyelectrolytes, the latter to ensure a bridging effect between particles and to enhance flocculation.

Clarifloc is added to the raw screened sewage to promote flocculation of the suspended and colloidal matter and is passed into coagulation tanks. The flocculated sewage then enters up-flow Clariflow tanks where a suspended sludge blanket is created. This acts as a filter maintained in position by a combination of gravity and upward flow. The blanket level is monitored continuously and desludged at regular intervals. Polyelectrolyte is added to the sludge before it is dewatered and disposed of to landfill.

The old sedimentation tanks at Sandown were used as polishing tanks which doubled the residence time and allowed 4 rather than 6 Clariflow units to be utilised.

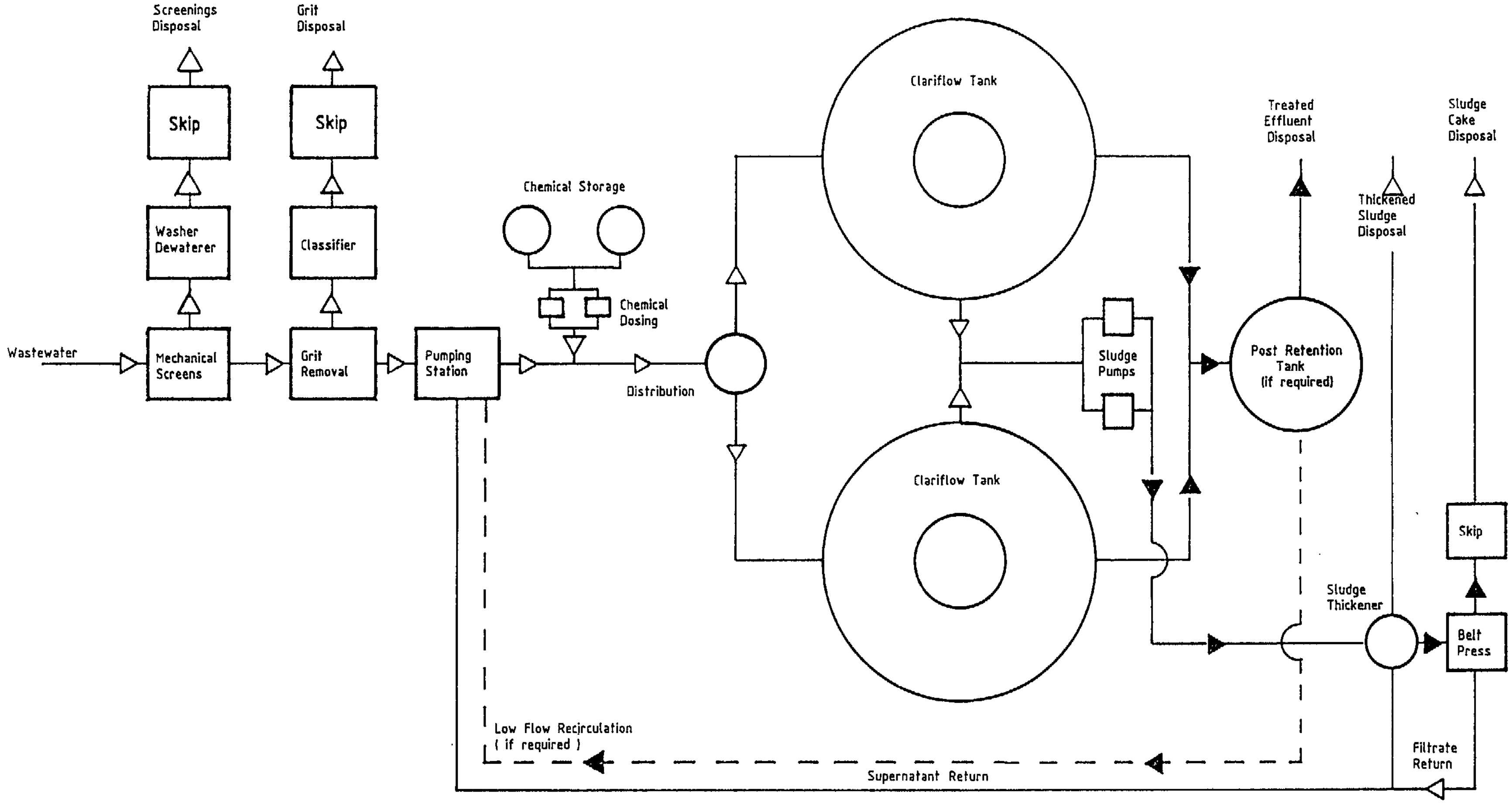


Fig 5.1 Process schematic for Clariflow disinfection plant at Sandown (courtesy Blue Circle Industries plc)

5.3. Disinfection efficiency

The Clariflow process achieves disinfection through a combination of blanket filtration and the effect of alkalinity. An evaluation of the process during commissioning at Sandown, involved eight 24h monitoring periods by Blue Circle, with discrete sampling conducted by Southern Water. Bacteriological data from the 24 h sampling runs and the discrete sampling show that faecal coliform reductions were proportional to pH (Tables 5.1 and 5.2). A 2 log removal could be achieved at pH 10.5 while >3 log removal was achieved at pH 11.0. The settled effluent refers to effluent from the process prior to the polishing tanks, whilst the final effluent was collected after polishing.

Bacteriological results from the Stander plant in South Africa, which operates a three stage lime clarification process, also indicate the enhanced removal of microorganisms at higher pH levels (Ronen, 1981). Reductions of 2 log total coliforms were obtained at pH >10.4, whilst enterococci and coliphages proved more resistant to lime treatment (Table 5.3). An earlier study at the same plant (Grabow et al, 1978) confirmed the higher efficiency at higher pH. Interestingly, percentage reductions for enteric viruses were much higher than those of the total plate count, coliforms and enterococci at all pH values. The results indicated that some bacteria may even multiply during lime treatment at pH 9.6. Laboratory studies showed that gram-negative bacteria were highly sensitive to lime treatment whilst the gram-positive bacteria, *Streptococcus faecalis*, *S. aureus* and *Bacillus* species, were much more resistant.

Viral and salmonellae assays at the Sandown plant (Table 5.4) indicated the complete removal of *Salmonella* at pH >9.5 but the Clariflow process appears less efficient for viral inactivation. In the viral assays, crude sewage samples proved toxic to the test cells and results were therefore limited.

Table 5.1: Results of 24 hour sampling of faecal coliforms in crude and final effluent at Sandown (Blue Circle, 1987)

	faecal coliforms ($100ml^{-1}$)			
pH	Crude	Settled	Final	log removal
8.5	1.46×10^7	1.16×10^7	1.38×10^7	0.02
9.0	1.6×10^7	8.7×10^6	1.24×10^7	0.11
9.5	2.12×10^7	7.2×10^6	4.3×10^6	0.69
10.0	2.52×10^7	6.2×10^6	3.8×10^6	0.82
10.0	1.66×10^7	2.2×10^6	1.2×10^6	1.14
10.5	2.99×10^7	2.1×10^6	7.2×10^5	1.62
11.0	2.24×10^7	2.0×10^6	1×10^4	3.35

Table 5.2: Results of spot sampling of faecal coliforms in crude and final effluent at Sandown (Harrington and Smith, 1987)

	faecal coliforms ($100ml^{-1}$)			
pH	Crude	Settled	Final	log removal
< 8.0	2×10^7	4.9×10^6	$> 3.7 \times 10^6$	0.73
8 - 8.5	1.5×10^7	4.7×10^6	4.6×10^6	0.51
8.5 - 9	2.4×10^7	$> 5.3 \times 10^6$	$> 4.6 \times 10^6$	0.71
9 - 9.5	1.6×10^7	4.3×10^6	2.5×10^6	0.81
9.5 - 10.5	3.9×10^7	$> 1.3 \times 10^6$	$> 8.5 \times 10^5$	1.66
> 10.5	3.2×10^7	$> 2.1 \times 10^5$	$< 5 \times 10^4$	2.81

Table 5.3: Removal of micro-organisms during lime treatment (Ronen, 1981)

Microorganism	pH range	Number of microorganisms		Log Reduction after clarification
		Influent	Effluent	
Total plate count (100 ml^{-1})	11.2-11.4	45 000	210	2.33
	10.4-10.5	31 000	800	1.59
	10.0-10.2	50 000	5 400	0.97
	9.6	37 000	26 000	0.15
Total coliforms (100 ml^{-1})	11.2-11.4	60 000	2 - 13	4.5-3.7
	10.4-10.5	145 000	680	2.33
	10.0-10.2	160 000	9 400	1.23
	9.6	155 000	71 000	0.34
Enterococci (100 ml^{-1})	11.2-11.4	-	-	-
	10.4-10.5	2 200	160	1.14
	10.0-10.2	2 270	420	0.73
	96	3 570	1 166	0.49
Coliphages (ml^{-1})	11.2-11.4	140	0.2	2.85
	10.4-10.5	29	0.5	1.76
	10.0-10.2	34	10	0.53
	9.6	33	16	0.31

Table 5.4: The effect of pH on the inactivation of viruses and salmonellae at Sandown (Harrington and Smith, 1987)

	Viruses (l^{-1})		Salmonellae ($100ml^{-1}$)	
pH	Crude	Settled	Crude	Settled
9.0	15.0	ND	present	present
9.5	ST	188	70	0
10.0	ST	235	-	-
10.5	ST	55	20	0

ND = not detected
ST = sample toxic

Lime has been used as a disinfectant for viruses in sludge for the inactivation of poliovirus, reovirus and parvovirus (Koch and Strauch, 1981) and at pH 12 has been shown to be effective against clostridial spores in sludge (Paulsrad and Eikum, 1983). In experiments conducted with raw domestic sewage, inoculated with poliovirus I, Sattar *et al* (1976) found that addition of lime to pH 11.5 resulted in a complete kill of virus in the supernatant after 1h. A 4-5 log reduction in viruses in the sludge was also achieved and further experiments suggested that the half-life of poliovirus in lime-sludge was not greater than 6h.

The possibility that bacteria may be stressed by the high pH treatment with a subsequently enhanced die-off rate in seawater has been investigated by the manufacturers of the Clariflow process. In a study on the decay rates of enteric bacteria in effluent from Sandown compared to untreated sewage, it was found that bacterial numbers declined in a logarithmic fashion with both time and cumulative radiation. In 5 out of 6 experiments it was found that coliforms (total and thermotolerant) from the Clariflow effluent died more rapidly than from crude sewage; the degree of stress appeared to be dependent on both pH and retention time (MEC, 1987).

A further study to establish the relationship between the concentration of Clarifloc and bacterial levels over a range of contact times showed that reduction in bacterial numbers increased with both Clariflow dose and contact time, though below pH 10, increased contact time had little added effect. Thus at pH 9.58, retention times of up to 6h resulted only in a 1 log reduction of thermotolerant coliforms and a 0.6 log reduction of faecal streptococci, whereas a 6h retention time at pH 11.04 resulted in a 3 log reduction in thermotolerant coliforms and 1.4 log reduction in faecal streptococci. The gram positive bacteria were observed to be more resistant to lime treatment throughout the study (MEC, 1988).

5.4 Factors affecting efficiency

It has been shown that bacterial inactivation is dependent primarily on pH and contact time (Sattar *et al*, 1976; Ronen, 1981; Harrington and Smith, 1987). However, there appears to be a minimum pH value (10) before the process becomes effective, even with long residence times. The pH is the most important parameter, as shown by the effective bacterial reductions at high pH (9-11). At lower pH., SS and BOD are efficiently removed; a low pH regime may thus be operated where physical rather than bacterial quality of the effluent is of greater concern. The pH is proportional to lime dosage and therefore has a significant bearing on costs.

Residence time is also a critical factor; despite approximately constant influent coliform levels at Sandown, the increased retention period at night led to a marked improvement in bacterial quality of the effluent (Harrington and Smith, 1987).

5.5 Toxicity and by-product formation

The Clariflow process has a potential environmental impact in terms of the pH of the discharged effluent. Although likely to be rapidly buffered by seawater, particularly at highly dispersive sites, it is possible that there may be a localised ecological effect at the discharge point. However there are no data available on this aspect from operation at Sandown. In addition it is one of the few disinfection processes which generates substantial quantities of a by-product requiring disposal. The major by-product formed is a relatively large amount of mainly inorganic sludge. It is removed from the base of the unit as a thick sludge and from the blanket as a low solids sludge (approximately 0.5 - 2% solids). The low solids sludge settles to approximately 15% solids and the combined sludge is filtered to form a filter cake (approximately 40% solids).

Although the mass of sludge on a dry solids basis may be 2.5 - 3 times normal sludge production, its dense nature means that the volume of sludge may only be slighter greater than the equivalent primary treatment sludge production. In chalk areas, such as Sandown, a high pH sludge may be unsuitable for agricultural use as a fertiliser and has to be disposed of to landfill instead. Enhanced removal of heavy metals from the effluent, which was observed at Sandown, may lead to their concentration in the sludge, and further limits its suitability for agricultural use.

5.6 Costs

5.6.1 Capital costs

The Sandown plant was built in 1985 for a turnkey price of approximately £2.4 million, though this was totally inclusive of all civil engineering requirements. The true capital costs were nearer £1.8 million and included the inlet works as well as the sludge handling system. Blue Circle also produce a $60 ls^{-1}$ single module for uprating small works at a cost of £300,000 - £400,000.

5.6.2 Operating costs

The costs outlined here are specific to Sandown; costs for other sites will tend to vary with the nature of the sewage to be treated.

Operation and maintenance costs include those of chemical and power consumption and sludge handling including polyelectrolyte addition, dewatering and transport.

a) Clarifloc EM40 costs £58.40 $tonne^{-1} \equiv$ £75.34 m^{-3}

The chemical costs will obviously depend on dose.
From 6 months at Sandown, operating over a pH range of 9-11:
@ Chemical dose = 0.17 - 0.83 ml l^{-1}; cost = 1.28 - 6.25pm^{-3}

b) Power costs @ 3.25p kwh^{-1}; cost = 0.32 - 0.62pm^{-3}

Thus total operation and maintenance costs range from 1.9 - 6.57 pm^{-3} though for higher pH levels, costs = 4 - 6.5 pm^{-3}.

5.7. Conclusions

1. At high pH levels (>10), the Clariflow process is capable of 2 - 3 log reductions in faecal coliforms and in addition stresses the microorganisms so that the subsequent die-off rate is enhanced. The process appears to be less effective as a virucide but available results are limited.

2. Though the effluent is quickly buffered by seawater, the high pH of the treated effluent may cause a localised ecological impact.
The process also generates a substantial amount of sludge by-product (588 tonnes/month in July). Due to the high lime content and possible contamination by metals and organics, this may be unsuitable for utilisation on land and at Sandown is disposed of to landfill.

3. Capital costs are fairly high; £1.8M for the Sandown plant of 21,000 m^3d^{-1}. Blue Circle supply a 60 ls^{-1} module for uprating small works. Operating costs mainly arise from chemical consumption, the Clarifloc dose being proportional to efficiency and power. Since it may only be necessary to treat the sewage during the bathing season, there is scope for operation at lower pH in winter with lower costs.

Experimental Disinfection Techniques

6. CHLORINE DIOXIDE

6.1 Introduction

Chlorine dioxide has been used extensively as a drinking water disinfectant in Europe and the US, particularly for the control of phenolic or algal tastes and odours. It is a more efficient disinfectant than chlorine especially with regard to viruses, and has the important advantage of a lack of reaction with ammonia and insignificant halogenated organic compound formation. However, it has yet to be used as a wastewater disinfectant, despite pilot studies which suggest that it would perform effectively. This is largely due to the fact that it is a potentially hazardous gas, which necessitates its generation on-site, and it has high operating costs associated with the feed chemical sodium chlorite.

With no operating experience of chlorine dioxide wastewater disinfection, it is difficult to assess the environmental impacts. Adverse ecological effects may arise from its inorganic by-products but these remain to be fully evaluated. Unless chlorine dioxide can be shown to exhibit fewer adverse health and environmental effects than alternative disinfectants, the high costs associated with its production suggest that it is likely to remain an experimental wastewater disinfectant only.

6.2. Production and application

Chlorine dioxide is a hazardous gas with a lower explosive limit of 10 - 39% in the vapour phase. For this reason it is produced *in situ* from the reaction of sodium chlorite ($NaClO_2$) with either chlorine gas or hydrochloric acid. The most common method of production in the US is the chlorine-chlorite process, though a few European potable water treatment plants use the acid-chlorite process. With both methods the chlorine dioxide is produced as a solution which avoids the danger of handling chlorine dioxide gas.

6.2.1 The chlorine-chlorite process.

$$Cl_2 + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl$$

When the chlorine-chlorite method is used, sodium chlorite is supplied as a powder or concentrated solution, whilst a solution of chlorine gas in water is produced in an analogous manner to that used in chlorination. Excess chlorine is needed to achieve high yields of chlorine dioxide, though the presence of unreacted chlorine in the product solution tends to defeat the object of using chlorine dioxide as an alternative disinfectant, if unreacted chlorine is available for organochlorine compound formation. Alternatively, reaction of the correct stoichiometric ratio of feed chemicals, at low pH, achieves more efficient conversion to chlorine dioxide (EPA, 1986).

A system that reacts aqueous sodium chlorite with chlorine gas under vacuum has been developed, which can be easily integrated using existing chlorine equipment. The delivery of the feed chemicals and reaction under vacuum eliminates the explosive hazard associated with pressurising chlorine dioxide gas. The process has been found to produce chlorine-free chlorine dioxide in 95-98% yields (Aieta and Roberts, 1981).

6.2.2 The acid-chlorite process.

$$4HCl + 5NaClO_2 \rightarrow 4ClO_2 + 5NaCl + 2H_2O$$

There is considerably less operating experience of this method. Though the on-site generation of chlorine dioxide minimises the transport hazards, there still remains a possible safety hazard in the handling of two potentially dangerous chemicals.

6.3. Chemistry

Chlorine dioxide is a neutral compound of chlorine existing in an oxidation state of IV, and is considered to be a stable free radical. Unlike chlorine, chlorine dioxide does not undergo hydrolysis in water, remaining intact over the pH range 4 - 8.4. However it disproportionates at elevated pH, in aqueous solution, to form the inorganic ions chlorite, ClO_2^-, and chlorate, ClO_3^-. These species exhibit no bactericidal activity and their formation therefore results in a loss of disinfectant capacity. The chlorite ion is also a major by-product of the reaction of chlorine dioxide with organic compounds. Unlike chlorine, chlorine dioxide generates no by-products such as THMs or chloramines, but its powerful oxidising capacity enables it to react with a wide range of organic compounds.

6.4. Mechanism of inactivation

6.4.1 Bacteria

Roller and Olivieri (1980) conducted experiments on whole cells of the bacterium, *Haemophilus influenza*, to investigate the inactivation mechanism of chlorine dioxide. There appeared to be no loss of DNA transforming activity, and total inhibition of the dehydrogenase enzymes did not result in cell death. Protein synthesis was partially inhibited but not sufficiently to account for inactivation. It was concluded that bacterial inactivation appeared to occur other than via enzymes, protein synthesis or DNA, although the inhibition of protein synthesis may have had a contributory effect.

6.4.2 Viruses

The mechanism of viral inactivation by chlorine dioxide is thought to differ from that of chlorine in that the viral capsid rather than the nucleic acid is the target. Virus inactivation has been found to occur as a result of chlorine dioxide reaction with discrete chemical moieties in the viral protein, whilst experiments with f_2 bacteriophage suggest that a reaction with tyrosine residuals was responsible (Noss *et al*, 1986).

6.5. Disinfection efficiency

Chlorine dioxide is both a powerful bactericide and virucide, proving to be a better disinfectant than chlorine over a wide pH range. It also appears to be more efficient at the higher pH associated with wastewater disinfection. A characteristic of chlorine dioxide disinfection is its speed of reaction and the low dosages necessary for inactivation.

In one of the most comprehensive studies on the use of chlorine dioxide in wastewater disinfection (Roberts, 1981), it was shown to be generally superior to chlorine on the basis of (residual x time) product, with a residual of 0.33 mgl^{-1} of chlorine dioxide necessary to achieve 1000 total coliforms $100ml^{-1}$ in activated sluge effluent, compared to 0.9 mgl^{-1} for chlorine. This has also been confirmed in experiments on biologically treated domestic effluent by Fressonnet-Chambarlhac *et al* (1983a). To obtain a 3 log reduction in faecal coliforms a much shorter contact time and residual level was needed for chlorine dioxide than chlorine (Table 6.1).

Table 6.1. Dose of disinfectant required to attain a 3 log reduction in faecal coliforms (Fressonnet-Chambarlhac *et al*, 1983a)

	Dose (mgl^{-1})	Contact time (min)	Residual concentration ($mg^{-1}l$)
ClO_2	4.5	10	0.7
Cl_2	3.5 -4.1	40	2 - 2.6

Contrary to the results of these studies, Aieta *et al* (1980) found that when compared on a mass dose basis at 30 min contact time, the performance of chlorine dioxide and chlorine as bactericides in secondary effluent was almost identical. However, chlorine dioxide required a shorter contact time to achieve inactivation.

Table 6.2 is a compilation of reported disinfection efficiencies for chlorine dioxide. In comparison with analogous data for chlorine, it is evident that high inactivation efficiencies are achievable at relatively low dosages and/or contact times. In the comparison of results of different studies a number of factors should be considered, particularly the use of pure cultured organisms rather than natural populations; the varying quality of the wastewater effluent; and the use of different enumeration techniques for the microorganisms. However most researchers are in agreement that chlorine dioxide is a more potent virucide than chlorine, which suggests that the use of accepted indicator organisms yields conservative performance data for chlorine dioxide disinfection in secondary effluent (Aieta *et al*, 1980).

Studies on viral inactivation in combined wastewater flows by Tifft *et al* (1977), showed that 4-5 log reductions may be achieved with 12 mgl^{-1} chlorine dioxide in 2 min contact time. Although viruses are generally less susceptible to disinfection than bacteria, the dose required to reduce virus levels relative to indicator organisms is much smaller than it is for chlorine, as shown in Table 6.3.

In trials conducted in secondary effluent to asssess the virucidal efficacy of chlorine dioxide compared to chlorine, Aieta *et al* (1980) demonstrated that chlorine dioxide is a more effective virucide than a bactericide, and over a short contact period proves more efficient than chlorine in inactivating poliovirus I and *in situ* coliphage.

Table 6.2. Chlorine dioxide doses and contact times necessary to inactivate various microorganisms

Microorganism	Dose (mgl^{-1})	Residual (mgl^{-1})	Contact time(min)	Log reduction	Reference
faecal coliform	4.5	0.7	10	3	Fressonnet *et al* (1983a)
enterovirus	1.73 - 6.51		15	0.45 - 1.58	
coliphage	1.73 - 6.51		15	2.1 - 3.16	
faecal coliform	5		3	4.7	Longley *et al* (1980)
f_2 bacteriophage	5		3	2.4	
total coliform	2		5	1.34	Roberts (1981)
	5		5	3.01	
	10		5	4.4	
	2		10	1.43	
	5		10	3.69	
	10		10	5.09	
	2		30	1.61	
	5		30	3.50	
	10		30	5.81	
total coliform	12		2	3.39	Tifft *et al* (1977)
faecal streptococci	12		2	1.80	
poliovirus I	12		2	4.0	
bacteriophages:					
(0174)	12		0.5	5.4	
(f_2)	9		2	4.5	

Table 6.3. Relative doses of chlorine and chlorine dioxide (mgl^{-1}) required to achieve a similar reduction in numbers of microorganisms (Fressonnet-Chambarlhac *et al*, 1983a)

Disinfectant	faecal coliform	enterovirus	coliphages
Cl_2	1	4 - 20	4.5 - 10
ClO_2	1	2 - 3	1.5 - 2.6

Longley *et al* (1980) reported the relative biocidal efficiencies of chlorine and chlorine dioxide in inactivating indigenous faecal coliforms and coliphages in wastewater. Faecal coliform inactivation of at least 4 logs and coliphage of 3 logs were observed at 3 min contact time which greatly exceeded comparable chlorine inactivation of coliphage of approximately 2 logs.

6.6. Factors affecting efficiency

The efficiency of chlorine dioxide appears to be less susceptible to the effects of parameters such as pH, solids and wastewater constituents, which would suggest that it is more suitable than chlorine as a disinfectant for wastewater, where large variations in these factors are encountered.

6.6.1 pH

Chlorine dioxide is less sensitive to pH changes than chlorine, thus at higher pH chlorine dioxide is a more effective disinfectant. However, at lower pH their efficiencies are comparable.

Studies by Noss and Olivieri (1985) showed that the bacteriophage

f_2 was inactivated by chlorine dioxide solutions at acid, neutral and alkaline pH, with the rate of inactivation increasing with increasing pH. However at elevated pH, where chlorine dioxide disproportionates, reduced virucidal efficacy was displayed; this appeared to confirm the theory that the radical species $ClO_2\cdot$ was the active disinfectant. Though increased efficiency at high pH is not generally observed for bacteria, the enhanced virucidal action at high pH has been confirmed by other researchers.

6.6.2 Contact time

A characteristic of chlorine dioxide disinfection is its speed of disinfection. A greater degree of inactivation can be achieved within a shorter time period than with chlorine (Roberts, 1981). An exception to this was observed in experiments on effluent which had undergone advanced wastewater treatment, where much of the ammonia-nitrogen and soluble organics remained. Long contact times of 15 - 30 min were found necessary for disinfection, since there was evidence that chlorine dioxide was present for 5 - 10 min with little or no virus inactivation (Warriner *et al*, 1985).

6.6.3 Wastewater constituents

One of the major advantages of chlorine dioxide over chlorine is that it does not react with ammonia to form chloramines and THMs. However there are a wide range of wastewater constituents which exert a very rapid demand on chlorine dioxide, reducing the concentration of disinfectant significantly. Chlorine dioxide appears to react instantaneously with organics, leading to a rapid formation of maximum organic halogen concentrations (Stevens, 1982). This is in contrast to chlorine reactions whereby a steady reaction with wastewater constituents over a period of time is reported (Jolley, 1975).

6.6.4 Suspended solids

As with all other disinfectants, the efficiency of chlorine dioxide in wastewater is limited by the aggregation of microorganisms and adsorption to suspended matter. High concentrations of solids offer physical protection to bacteria and viruses and possibly exert an additional chemical demand. The physical and chemical conditions that allow viral aggregation may also allow partially inactivated virions to reassociate and co-operatively infect host cells (multiplicity reactivation). This protective mechanism may be more important with chlorine dioxide because of its fast reactivity and consumption in competing reactions (Aieta *et al*, 1980).

6.7 Toxicity and by-product formation

6.7.1 Toxicity

There are a number of toxicological effects associated with chlorine dioxide and its byproducts, the inorganic ions chlorite (ClO_2^-) and chlorate (ClO_3^-), including haemolytic anaemia and methaemoglobinaemia. The haemolytic activity of chlorine dioxide and its derivatives is thought to be caused by the *in vivo* production of hydrogen peroxide, a mechanism common to most oxidants causing haemolytic anaemia (Bull, 1982). Effects are not always apparent in clinical tests. No adverse physical symptoms were detected in healthy male adults after 84d exposure to $5mgl^{-1}$ of chlorine dioxide, chlorite, or chlorate in drinking water. The exceptions were individuals deficient in a certain enzyme sensitive to haemolytic agents, who showed significant changes in blood and serum parameters (Lubbers *et al*, 1982; Bull, 1982). Studies have found no evidence for mutagenic activity of chlorine dioxide, chlorite or chlorate (Meier *et al*, 1985) and it has been shown that chlorine dioxide does not act as a tumor promotor or complete carcinogen (Condie, 1986).

The human health risks associated with the use of chlorine dioxide thus appear small. No information relating to potential effects on marine organisms was found.

6.7.1 By-product formation

Reduced production of THMs with chlorine dioxide disinfection has been demonstrated in studies on both potable water and wastewater (Chow and Roberts,1981; Roberts, 1981; Lykins and Koffskey, 1986).

In a comprehensive study on the use of chlorine dioxide as a wastewater disinfection, Roberts (1981) investigated halogenated by-product formation during laboratory disinfection of samples of wastewater effluents from treatment plants in California. One was an activated sludge effluent from the Palo Alto plant and the other an extended aeration activated sludge effluent from the Dublin San-Ramon plant. The latter produced a nitrified effluent which was subsequently filtered. The effluents were dosed with chlorine dioxide and chlorine at concentrations of 20 and 40 mgl^{-1} for 24 h and the increase during the 24h contact time of both total organic halogens and total THMs was measured.

As shown in Table 6.4, chlorine dioxide produced no significant increase in total organic halogen (TOX) or THMs in either nitrified or non-nitrified wastewater, and in some cases even reduced the level. Chlorine produced significant quantities of both TOX and THMs, particularly in the nitrified effluent because of the presence of the more reactive free chlorine residuals. Measurable quantities of TOX were formed in both wastewaters with chlorine dioxide, but inconsistently; this was thought to reflect natural variations in secondary effluent quality. Field trials on the two disinfectants subsequently confirmed the laboratory results. The doses and contact times given in Table 6.5 are those that achieved a similar reduction in bacterial numbers. Thus although chlorine dioxide has the potential to form halogenated organics, the concentrations generated would be substantially lower in comparison to chlorine disinfection.

Table 6.4. Increase in halogenated organics in laboratory trials of wastewater disinfection by chlorine dioxide and chlorine (Roberts,1981)*

Disinfectant	Dose mgl^{-1}	Non nitrified ($20-35\ mgl^{-1}\ NH_3-N$) TOX	THM	Nitrified ($< 1mgl^{-1}\ NH_3-N$) TOX	THM
ClO_2	20	0.3-3.0	-0.06-0.02	-0.2-0.5	0.01 -0.02
	40	-0.8-1.6	-0.02-0.10	1.4	0.03
Cl_2	20	6-10	0.18-0.53	19.3-22.4	3.75-3.97
	40	7.1-8.1	0.85-1.31	26.2	4.87

* Increase calculated as concentration (mgl^{-1}) measured after 24h less predisinfection concentration; negative values denote decrease

Table 6.5. Increase in halogenated organics in field wastewater disinfection trials with chorine dioxide and chlorine (Roberts, 1981)

	Dose (mgl^{-1})	Time (min)	Residual (mgl^{-1})	Increase in TOX ($umoll^{-1}$)	Increase in THM ($umoll^{-1}$)
ClO_2	3.1	55	0.1	0.4	-0.04
	2.3	46	0.6	-0.5	0.04
Cl_2	18.7	55	12.8	10.2	1.02
	19.6	49	1.0	8.1	0.95

Chlorine dioxide does not react with ammonia and only slowly with primary amines. However, it reacts with tertiary amines to form secondary amines and aldehydes with the formation of chlorite. Reaction with phenols occurs rapidly through a complex mechanism which may lead to the production of quinones, chloroquinones, chlorohydroquinones and chlorophenols. Ketones, aldehydes and alcohols are oxidised to carboxylic acids, whilst sulphydryl amino acids react to form cysteic acids. Additional reactions which may occur in wastewaters include conversion of unsaturated aliphatics to form dichloro-compounds, chloroketones, chlorohydrins then epoxides (WPCF,1986).

6.8 Costs

As part of an EPA study on wastewater disinfection, Roberts (1981) calculated costs of chlorine dioxide produced from sodium chlorite and chlorine, compared to chlorine disinfection for a range of plant sizes. The experiments were conducted at two wastewater plants in California the Palo Alto and Dublin San-Ramon plants. The figures presented here relate to a non-nitrified secondary effluent from the Palo Alto plant only, the wastewater characteristics of which are presented in Table 6.6. The disinfectant dosages to achieve a discharge requirement of 1000 total coliforms 100 ml^{-1} were determined (see Table 6.7). Roberts (1981) assumed a 100% conversion of sodium chlorite and 100% yield of chlorine dioxide based on sodium chlorite reaction with 4% excess feed. Thus 1.68kg of 80% sodium chlorite and 0.7kg of chlorine were required per kg of chlorine dioxide generated. Using the chemical feed costs shown in Table 6.8, the yearly chemical costs were calculated for a range of plant sizes. These, with the associated chemical costs, are presented in Table 6.9.

The price of dry sodium chlorite was found to be considerably lower ($\$2.67kg^{-1}$) than the solution, if purchased in drum quantities at January 1980 prices. The figures presented in Table 6.8 were thought to be conservative and it is possible that sodium chlorite could be purchased for between 45 - 60% of the price given.

Table 6.6. Wastewater characteristics of the activated sludge effluent from the Palo Alto plant (Roberts, 1981)

Wastewater	SS (mgl^{-1})	COD (mgl^{-1})	pH	log total coliforms ($100\ ml^{-1}$)
Unfiltered activated sludge	13.8	52.6	6.7 - 7.2	5.38

Table 6.7. Dose to achieve discharge requirement of 1000 total coliforms $100ml^{-1}$ in kgd^{-1} (Roberts, 1981)

Feed chemical	Plant size ($10^3\ m^3d^{-1}$)				
	3.78	18.9	37.8	189	378
chlorine dioxide	6.35	31.75	63.50	317.52	635.04
chlorine	8.17	40.82	81.65	408.25	816.48

Table 6.8. Chemical feed costs (1980 price basis) used to calculate the chemical costs of chlorine dioxide and chlorine production shown in Table 6.9 (Roberts, 1981)

	Unit cost ($\$kg^{-1}$)
Cl_2, 1 ton cylinder	0.342
Cl_2, rail cars	0.165
$NaClO_2$ (80%) < 250,000 lb/yr	5.99*
$NaClO_2$ (80%) > 250,000 lb/yr	4.36*

* based on manufacturers quotes for 25% $NaClO_2$ solution

Table 6.9: Annual capital and operating costs for chlorine and chlorine dioxide disinfection of secondary effluent for a range of plant sizes, to achieve a discharge requirement of 1000 total coliforms $100ml^{-1}$ (Roberts, 1981)

	Plant size (10^3 m^3d^{-1})									
	3.78		18.9		37.8		189		378	
$10^3\$y^{-1}$	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2
Contact basin	14.7	14.7	36.0	36.0	54.8	54.8	172.3	172.3	313.0	313.0
Generation and feed equipment	3.7	1.8	6.4	3.5	9.4	4.6	20.5	10.8	27.3	17.7
Operation and maintenance cost	7.1	6.0	10.0	7.9	12.2	8.6	25.0	15.5	33.0	23.0
Chemical: Cl_2	0.6	1.0	2.8	5.1	5.5	10.2	13.5	24.8	27.0	49.6
$NaClO_2$	22.9	-	114.6	-	229.2	-	849.9	-	1699.8	-
Total										
10^3y^{-1}	49.0	23.5	169.8	52.5	311.1	78.2	1081.2	223.4	2100.1	403.3
¢m^{-3}	3.5	1.7	2.5	0.77	2.2	0.55	1.56	0.3	1.5	0.3
pm^{-3} *	2.0	1.0	1.4	0.4	1.2	0.3	0.9	0.2	0.9	0.2

* conversion of 1981 US$ value at 1988 exchange rate of 1US$ = £0.57

Table 6.10. Chemical costs (1988 price basis) of chlorine and sodium chlorite used to derive costings in Table 6.11

Feed chemical	cost(£kg^{-1})	Reference
chlorine	0.43	ICI, 1988
sodium chlorite (26%)	0.625	Interox, 1988

Table 6.11. Annual chemical costs for chlorine dioxide and chlorine disinfection of a secondary effluent for a range of plant sizes (to achieve a theoretical discharge requirement of 1000 total coliforms $100ml^{-1}$)

Feed chemical	Plant size (10^3 m^3d^{-1})				
(10^3£y^{-1})	3.7	18.9	37.8	189	378
Chlorine dioxide:					
chlorine	0.7	3.5	7.0	35.0	70.0
sodium chlorite	7.5	37.3	74.7	373.3	746.6
Chlorine:					
chlorine	1.3	6.4	12.8	64.1	128.1
sodium chlorite	Not applicable				

It is evident from Table 6.9 that despite the lower dosages of chlorine dioxide necessary for disinfection, the high costs of the feed chemical, sodium chlorite, make overall costs per m^3 some 2 - 5 times higher than chlorine, which exhibits distinct economies of scale. However, production of sodium chlorite on a large scale may lead to reductions in cost and these figures are based on conservative estimates.

Using figures obtained from UK manufacturers (Table 6.10), an analagous calculation of chemical costs show that chlorine dioxide disinfection would be approximately 6 times more expensive than chlorine (Table 6.11).

Estimates made by Rivoal (1983) for a wide range of disinfectants found capital costs for chlorine and chlorine dioxide disinfection to be of a comparable magnitude, whilst operating costs were 1.5 - 2.5 times as high for chlorine dioxide and comparable to those of chlorination/dechlorination. Total annual costs per m^3 were between 1 and 2 times higher.

6.9 Conclusions

1 Chlorine dioxide is an effective disinfectant over a wide pH range, with improved virucidal properties in comparison with chlorine. This suggests that the use of accepted indicator organisms may give conservative performance data for chlorine dioxide disinfection in secondary effluent.

2 Chlorine dioxide does not produce THMs and exhibits a low halogenated organic compound formation potential in comparison with chlorine. However, the inorganic products could exert adverse toxicological effects which may be critical for certain individuals sensitive to haemolytic agents. No environmental impact assessment has been conducted with regard to marine discharge.

3 Disinfection with chlorine dioxide would be 2 - 5 times more

expensive than chlorination because of the high costs of the feed chemical sodium chlorite. It would be more competitve when compared with chlorination/dechlorination for environmentally sensitive discharge sites.

4 It is an extremely hazardous gas with explosive properties. There are risks associated with handling the two potentially dangerous feed chemicals.

5 Though used extensively as a drinking water disinfectant and to control tastes and odours, chlorine dioxide has not been adopted as a wastewater disinfectant. This would appear to be due to a lack of existing performance data and because of cost and safety considerations.

7. PERACETIC ACID

7.1 Introduction

Peracetic acid (PAA) is a water soluble liquid which exists in equilibrium with hydrogen peroxide, acetic acid and water. It is an effective disinfectant which is currently used on a small scale for sterilisation in the dairy and brewing industries. Its high costs have generally precluded a wider application.

Pilot trials have been conducted by the manufacturers to establish its efficacy for sewage disinfection. Whilst the results appear promising, the short duration of the studies to date do not permit any firm conclusions to be drawn. PAA is a powerful oxidant which is capable of reacting with organic compounds in wastewater. In addition it is known to be a highly toxic substance and the possibility of the formation of organic derivatives with possible ill-effects has not yet been fully evaluated.

7.2 Production and application

Peracetic acid (PAA) is produced in the UK solely by Interox, under the trade names Proxitane and Oxymaster. Each disinfectant within this range contains different concentrations of PAA, hydrogen peroxide, acetic acid and water. Oxymaster, the product proposed for sewage disinfection, comprises (w/w):

12% peracetic acid
20% hydrogen peroxide
16% acetic acid
52% water.

A variety of packs (eg 30 kg or 200 kg) may be used for the supply of Oxymaster. Alternatively, it may be delivered in purpose-built tanks of 18 tonne loads. It is then transferred to bulk storage tanks of 316L steel and may be applied using a stainless steel metering pump and discharged via polythene and stainless steel downpipes. The rate of addition can be controlled by use of an automatic sampling and analysis device which measures residual PAA after approximately 90s, to establish a control loop.

The only materials recommended for prolonged contact with PAA are stainless steel 304L, 316L and PTFE, whilst soft PVC and polyethene are suitable for limited periods.

7.3 Mechanism of inactivation

Peracetic acid is a powerful microbiocide; with the peracid species being the active disinfectant. The mechanism of disinfection is thought to be through disruption of the sulphydryl and disulphur bonds within enzymes, which form important components in the cell membranes. Dislocation of the chemiosmotic function of membrane transport causes rupturing of cell walls and prevents cellular activity. Oxidation of essential enzymes within cells, thus impairing active transport across membranes and affecting intracellular solute levels, is also likely (Fraser, 1987).

Hydrogen peroxide also attacks cell membranes, through the action of hydroxyl radicals oxidising sulphydryl and hydroxy groups and double bonds in the protein/lipid layer. One important advantage of PAA over hydrogen peroxide is that it is not destroyed by catalase, an enzyme which detoxifies hydrogen peroxide and enables active growth of cells.

7.4 Disinfection efficiency

Typical reductions for *E. coli* for a range of effluent qualities are shown in Table 7.1 (Fraser, 1987). It was shown that a 3 log reduction in coliform bacteria required 19.5 mgl^{-1} PAA and 5 min contact time in crude sewage and primary effluent, whereas the same reduction could be achieved in 12s with 2 mgl^{-1} PAA in secondary effluent.

Table 7.1 Reduction of microorganisms with PAA for a range of effluent qualities (Fraser, 1987)

Wastewater treated	PAA dose (mgl^{-1})	Contact time (min)	Concentration of microorganisms		
			initial (cfu 100ml^{-1})	final	% reduction
Raw sewage 1	9.7	5	*6.7x10^{7}	1.9x10^{4}	99.97
	19.5	5	*6.7x10^{7}	1.5x10^{3}	99.99
Raw sewage 2	9.7	5	*6.0x10^{3}	<1.0x10^{2}	>98.3
Primary effluent	9.7	5	*4.6x10^{6}	9.4x10^{4}	98.0
	19.5	5	*4.6x10^{6}	9.0x10^{3}	99.80
	2.3	10	5.0x10^{6}	9.0x10^{5}	82.0
	4.6	10	5.0x10^{6}	1.0x10^{6}	80.0
	9.3	10	5.0x10^{6}	1.9x10^{4}	99.62
Secondary effluent percolating filter treatment	1.0	0.2	7.7x10^{4}	7.5x10^{4}	3.0
	2.0	0.2	1.7x10^{5}	2.0x10^{2}	99.88
	2.0	0.2	1.3x10^{5}	2.1x10^{3}	98.4
Secondary effluent activated sludge treatment	1.0	0.2	2.0x10^{5}	6.9x10^{4}	66.0
	2.0	0.2	2.9x10^{5}	3.0x10^{2}	99.60
	2.0	0.2	8.7x10^{4}	1.0x10^{2}	99.89

microorganism concentration refers to *E.coli* except:

* total viable count (37°C after 48 hours)

The activity of PAA as a bactericide depends to some extent on pH. As with many organic acid biocides (eg hypochlorous acid) the antimicrobial activity of the undissociated acid is greater than the anion formed on dissociation, thus it is less effective at higher pH. This has been confirmed by investigations on the bactericidal, fungicidal and sporicidal properties of PAA by Baldry (1983). Investigation of the time required for a complete kill of various bacteria, at pH 5, 6.5 and 8.0, showed that this increased with increasing pH. However, at each pH value, 5mgl^{-1} PAA was not always effective within 30 min; 25.1 mgl^{-1} was effective within 10 min and 98.8 mgl^{-1} was effective under 1 min in all cases. The effect of decreasing efficacy with increasing pH was also demonstrated by the effect of PAA on yeasts.

PAA is less effective as a virucide and sporicide than as a bactericide. The concentrations and contact times required for inactivation are shown in Table 7.2. A 3 log reduction in bacteria could be attained in under 5 min with a dose of approximately 10 mgl^{-1} whereas bacterial spores required 375 mgl^{-1} and 1 h contact time for equivalent reduction.

Table 7.3 summarises the efficacy of PAA as a virucide. The data reported from various studies show the wide range of responses of different viruses and the relatively high dosages required for inactivation. The results indicate that doses of PAA as high as 100 mgl^{-1} are necessary to achieve efficient inactivation of viruses. This is in contrast to its marked bactericidal properties.

Harakeh (1987) found considerable variation in the degree of resistance of several viruses with echovirus the most and simian rotavirus (SA11) the least resistant. Up to 140 mgl^{-1} PAA with 30 min contact time was necessary to give a 4 log reduction of

Table 7.2: Concentrations of PAA required for bacterial and sporicidal inactivation (Baldry, 1983)

Microorganism reduction	conc. PAA (mgl^{-1})	contact time (min)	influent (cfu (100ml^{-1})	effluent (cfu 100ml^{-1})	log red^n
Bacillus subtilis	375	60	1.9x10^5	2	4.97
spores	375	60	2.4x10^5	300	2.9
Legionella pneumophila	6	60	4x10^6	0	6.6
Saccharomyces Cerevisiae NCYC 762	10	>30			6
Total viable count	9.7	5	6.7x10^4	1.9x10^4	3.55
E.coli	2.0	0.2	2.9x10^5	3.0x10^5	2.99

Table 7.3: Concentrations of PAA necessary to achieve a 3-4 log virus reduction

Concentration PAA (mgl^{-1})	Contact time (min)	Microorganism	Reference
1900	5	poliovirus I adenovirus coxsackie B virus echovirus	Kline and Hull (1960)
380	1	classic fowl plague	Kapitancik (1973)
100	4	coxsackie A herpes	Bansemir *et al* (1979)
1000-2000	<30	SV40 poliovirus coxsackie B	
1000		hepatitis B	
1-100		bacteriophage poliovirus coxsackie echovirus	Fleming (1984)
140	30	human rotavirus	Harakeh (1987)
20	30	simian rotavirus(SA11)	

human rotavirus whilst only 20 mgl^{-1} was required for a similar reduction in SA11. At lower concentrations of PAA there was a characteristic biphasic mode of inactivation, with the majority occurring within 5 min. The sensitivity of human rotavirus and SA11 were markedly different, a concentration at which 50% of the human rotavirus survived led to a greater than 4 log reduction of SA11 within 5 min.

In a study sponsored by Interox (Brussels), it was found that PAA achieved similar reductions in bacteria as chlorine, with 5 mgl^{-1} of disinfectant achieving a 2 log reduction in 15 min (Depre, 1982).

7.5 Toxicity and by-product formation

7.5.1 Toxicity

Both PAA and hydrogen peroxide are extremely toxic. Toxicity tests on a variety of organisms have been commissioned by Interox to determine the LC_{50} (lethal concentration for 50% of a population) at various exposure times and the EC_{50} (concentration which causes a specific effect in 50% of organisms) in a variety of marine organisms.

The effect of Oxymaster on plaice (*Pleuronectes platessa*) and brown shrimp (*Crangon crangon*) under semi-static conditions is shown in Table 7.4. The LC_{50} values of approximately 10 mgl^{-1} are equivalent to dosages used in practice. Although residual levels of this order are highly unlikely to be encountered at the site of an outfall, this indicates the potential for toxic effects arising from exposure to unreacted PAA.

Similarly, the effects on the development of common mussel embryos (*Mytilus edulis*) Fairhurst, 1987 and pacific oyster embryos (*Crassostrea gigas*) Butler, 1987 to the D stage were assessed after a 48 h exposure period using concentrations of 0.006, 0.012,

Table 7.4: Lethal dose (LC_{50}) of PAA for plaice and brown shrimp at various exposure times (Tinsley and Sims: 1987a,1987b)

Time (h)	Effect on plaice PAA (mgl^{-1})		Effect on brown shrimp PAA (mgl^{-1})	
	LC_{50}	95% confidence	LC_{50}	95% confidence
24	11.8	10.7-13.5	35.3	39.8-54.7
48	10.7	9.6-11.9	20.7	17.9-24.0
72	10.7	9.6-11.9	16.6	14.1-19.4
96	10.7	9.6-11.9	15.2	12.9-17.9

Table 7.5: Effect concentration of PAA on the development of common mussel and pacific oyster embryos in terms of larval survival and development (Butler,1987; Fairhurst,1987)

	Common mussel	Pacific oyster
	PAA concentration (mgl^{-1})	
EC_{50} (development to D stage)	0.26 ± 0.05	0.27 ± 0.02
Highest 'no effect' concentration	0.12	0.12
Lowest concentration resulting in complete failure	1.8	1.8

0.12, 0.6 and 1.8 mgl^{-1} of PAA (Table 7.5). The concentration of PAA resulting in a 50% reduction in the success of larval development was 0.26 mgl^{-1} and 0.27 mgl^{-1} for the common mussel and pacific oyster respectively. Effects were observed at concentrations down to 0.12 mgl^{-1}. The lowest concentration at which embryo development failed completely was reported to be 1.8 mgl^{-1} PAA.

Work carried out by Plymouth Marine Laboratories has indicated that the residual toxicity of PAA is comparable to chlorine, both compounds giving similar acute toxicity curves. Concentrations of 0.15 PAA (mgl^{-1} Oxymaster) were found to be significant in toxicity tests although the LC_{50} dose was below the limit of chemical detection.

Studies on the mutagenicity of PAA (Agnet *et al*, 1976; Yamaguchi and Yamashita, 1980; Coppinger *et al*, 1983) appear to show conflicting results but these may be due to differences in the type of system used, which varied from bacterial to mammalian cells. PAA was found to induce forward mutations in *Salmonella typhi* (Agnet *et al*, 1976) whilst it was concluded by Coppinger *et al* (1983) in studies on unscheduled DNA synthesis and DNA repair, that PAA does not induce DNA repair in cultured human fibroplasts. PAA is thought to be a cancer initiator rather than promoter; with other mutagens it gives additive rather than synergistic effects. Although concentrations are likely to be low, this aspect could be of significance in the event of overdosing or spillage. The presence of hydrogen peroxide is also of concern, since its ability to damage DNA and its teratogenic properties are well documented.

7.5.2 By-product formation

The formation of toxic organic derivatives through the action of Oxymaster on biological organic substrates is thought to be extremely unlikely at the application concentrations used

(Fraser, 1987). It has been anticipated by Interox that whilst mild oxidation with highly oxidisable species such as sulphides may be expected, the formation of epoxides, peroxyaldehydes, peroxyacids or ketoperoxides is highly unlikely. The formation of free hydrogen peroxide is thought to be of greater likelihood. During trials with PAA (see Section 7.6.1), this was detected in secondary effluents at concentrations of 0.1-1 mgl^{-1}. It was observed, however, that the presence of hydrogen peroxide could be derived from its use in washing powders; low levels of hydrogen peroxide are also produced naturally by biota in aerobic systems (Fraser, 1987).

However, the absence of PAA and hydrogen peroxide in seawater during dosing of PAA may be due to the lack of sensitivity in the titrimetric analytical methods employed. Given the highly reactive nature of PAA and hydrogen peroxide it is reasonable to assume that some peroxylated compounds will be formed in reaction with the matrix of organic precursors in sewage effluent. During trials conducted in conjunction with Anglian Water in 1987 (see Section 7.6.2), GC/MS analyses of the crude and dosed sewage showed no evidence of any gross chemical changes before, during or after disinfection. However, it was observed that high levels of fats and oils present in the effluent may have obscured any subtle chemical changes. The concentrations of any potential by-products and the associated risk to biota arising from the large-scale use of PAA remains to be quantified (MAAF, pers. comm.).

Peracids are known to be excellent donors of oxygen atoms to amines producing amine oxides from tertiary amines and hydroxylamines from secondary amines (Roberts and Casiero, 1977). However it is the formation of epoxides which is of greatest concern, produced by the oxidation of alkenes with peroxyacids and peroxides. Epoxides are effective mutagens and are able to induce a range of genetic effects including cancer. Case control studies of cancer incidence show in certain work environments (eg where ethylene oxide is used for sterilisation) an epoxide is the sole or predominating mutagen/carcinogen (Ehrenberg and Hussain, 1981) There is also concern that through free radical formation, chlorine may be generated from seawater, which could become involved in organic reactions to producing carcinogenic THMs.

7.6 Pilot studies

7.6.1 Plymouth (Interox/South West Water)

In 1987, trials using PAA as a sewage disinfectant were undertaken by Interox, in conjunction with South-West Water, to evaluate whether the bathing water quality at Plymouth could be sufficiently improved to satisfy EEC bathing water quality standards.

Plymouth and the surrounding areas are served by a number of sewage treatment works, though sewage from the City centre (approximately 11 million m^3y^{-1} from a population of 86400) is discharged untreated. Based an preliminary results of laboratory experiments, field trials were conducted using doses of 20, 15 and 10 mgl^{-1} PAA applied to the 5 separate sewerage systems discharging into the main outfall. Coliform samples were taken in the sewage, at the beach and in the discharge plume.

The results of the sewage sampling are shown in Table 7.6 which shows that treatment with 15 mgl^{-1} PAA led to a typical 1.5 log reduction in coliforms. Samples of seawater were obtained daily from points along the shore which were identical to those used by Plymouth City Council to monitor the compliance of their bathing beaches with the EEC Directive. The failure rate was found to be 29% in 1986/7, which was not significantly different from the figure of 20% obtained by Interox prior to the trial. Following disinfection, the failure rate was 1.5% (2 out of 131 samples) for the 10d when the higher PAA doses were applied. At the lower 10 mgl^{-1} dose, the overall failure rate increased to 11%. However,

Table 7.6: Mean coliform values in sewage before and after disinfection with 15 mgl^{-1} PAA during Plymouth trials (Interox/SWW, 1987).

Sewage	Mean total coliforms ($cfu100ml^{-1}$)		Mean faecal coliforms ($cfu\ 100ml^{-1}$)	
	arithmetic	geometric	arithmetic	geometric
Untreated	$3.4x10^7$	$7.8x10^6$	$8.1x10^6$	$2.4x10^6$
Treated	$6.8x10^6$	$1.9x10^5$	$2.6x10^6$	$7.4x10^4$
log reduction	0.7	1.6	0.5	1.5

Table 7.7: Effect of PAA disinfection on rate of compliance with EEC bathing water quality standards in sewage plume and seawater at Plymouth (Interox/SWW, 1987).

Sample	No treatment		20/15 mgl^{-1} dose		all doses	
	failure rate*	(%)	failure rate	(%)	failure rate	(%)
Background	29/105	28	13/132	10	25/160	16
Discharge plume	95/135	70	76/170	45	95/206	46

* = no of failures/no of samples

% = % failure rates

the short duration of the trial and the dependence of bacteria concentrations on weather conditions, tidal currents and the presence of other discharges into the Sound, did not allow a direct correlation between Oxymaster dosing and any improvement in water quality to be established.

The results of the sewage plume sampling are shown in Table 7.7. Because of the influence of other discharges into Plymouth Sound, background samples were taken when no sewage was being discharged at the Rusty Anchor outfall. The results show that during disinfection trials the background failure rates were significantly reduced at the higher doses. This may have been coincidental, although it is possible that disinfection may have reduced the background levels. Failure rates in the discharge plume were also significantly reduced from 70% to 45%.

A statistical analysis of the results to estimate whether disinfection produced statistically significant differences in the levels of bacteria, showed that PAA achieved significant reductions in 17 out of 48 cases. Faecal coliform reductions were significant in 4 beach and 3 plume samples whilst total coliform reductions were significant in 6 beach, 2 background and 2 plume samples.

PAA and hydrogen peroxide were found to be absent in sewage samples over the entire experimental period and results indicated that there was a rapid depletion of disinfectant even before dilution. Background levels of residual peroxygen in sewage and disinfected sewage were determined and compared with results obtained from a patented PAA test kit, which has a detection limit of <0.5 mgl^{-1} total peroxygen. However the titrimetric devices used for analysis were unlikely to be sensitive enough to detect low concentrations in the sewage plume or seawater.

At dose levels of 20 and 15 mgl^{-1} PAA, disinfection of 2 - 3 log reductions of coliforms was achieved in up to 100,000 m^3d^{-1} of raw sewage. At dose levels of 10 mgl^{-1} inadequate disinfection was achieved. Whilst levels of faecal coliforms in the background waters were also reduced and there was a reduction in the number of beach samples failing to meet EEC standards, it was not possible to establish a firm causal link between disinfection and reduced failure rate, due to the influence of factors such as tidal currents and other discharges.

7.6.2 Clacton (Interox/Anglian Water)

In November/December 1987, a 6 week study was conducted in conjunction with Anglian Water, at a new sewage works at Clacton. This works receives domestic effluent with some metal-plating waste; the sewage is comminuted before discharge.

PAA was dosed upstream of comminution and monitoring at the end of the 800m outfall was undertaken for thermotolerant coliforms and faecal streptococci, with additional viral determinations. Although the results are not yet generally available, preliminary results showed that PAA was effective for thermotolerant coliforms giving 2-3 log reductions, but less effective for faecal streptococci and enteroviruses, giving only 1-2 log reductions. The short retention time (90s) and high organic load are thought to have adversely affected the performance. In addition GC/MS analyses were conducted on both crude and dosed sewage, which showed no change in the chemical composition before or after disinfection. However, any subtle chemical changes may have been obscured by the high levels of fats and oils in the sewage effluent.

7.6.3 Bishopston (Welsh Water)

Welsh Water conducted sewage disinfection trials over the period 1977-1979. Laboratory tests and pilot trials established chlorine and PAA as suitable agents for disnfection which were subsequently chosen for field trials at two sites on the South

Welsh coast (see Section 2.10.2). Pilot studies on a 30:20 standards activated sludge effluent from the works at Bishopston established that 4 mgl^{-1} PAA was necessary to achieve a 3 log reduction of *E.coli* in 30 min which, on dilution, would achieve compliance with the EEC standards. Although no biological studies were conducted on the environmental impact of PAA due to the late start up of the trial, it was thought that the potential formation of epoxylated compounds may have a deleterious effect on marine organisms. It was concluded that PAA would be an effective but expensive disinfection option.

7.6.4 Weston-Super-Mare (Interox/Wessex Water)

Trials were conducted by Wessex Water at Weston-Super-Mare to establish the efficacy of PAA (either synergistic or additive) alongside the existing hypochlorite disinfection system (see Section 2.11) and with PAA alone. Provisional results showed that the addition of 6-10 mgl^{-1} PAA permitted a reduction in chlorine dosing while achieving an equivalent inactivation efficiency. However, due to technical problems the results were not considered sufficiently conclusive to warrant conversion to the more costly PAA system. Although the smaller volumes required in comparison to chlorine were attractive, the potential cost increase of 20% (£30,000 over a 20 week season) was undesirable.

7.7 Costs

Capital costs for PAA application are low. They include storage tank, dosing pumps, data loggers and on-line monitoring facilities. Operational costs are primarily the chemical costs which depend on the sewage flow and quality.

Costs calculated for a range of effluent qualities are reported by Interox in Table 7.8. The January, 1988 costs of Oxymaster (12% w/w PAA) were reported at £780 $tonne^{-1}$ for requirements exceeding 800 tonnes per year and £800 $tonne^{-1}$ for supply of 500 tonnes per year.

Table 7.8: Oxymaster (12% w/w PAA) application costs for various wastewater qualities (Interox, 1988).

Wastewater quality	Highest dose Oxymaster (mgl^{-1})	cost (pm^{-3})	volume to disinfect $1m^3$ sewage	Ratio sewage: Oxymaster
strong raw sewage	125 (15)*	9.7	114ml	8772:1
normal raw & settled sewage	100 (12)	7.8	90.9	11000:1
effluent	33 (4)	2.6	30ml	33333:1
poor quality effluent	50 (6)	4	45ml	22222:1

* figures in parentheses represent equivalent doses of PAA

7.8 Conclusions

1 PAA is an effective bactericide, characterised by its fast action, but is less effective for more resistant microorganisms such as viruses and bacterial spores.

2 PAA is a flexible disinfectant suitable for emergency situations and for application to all sewage types.

3 Both PAA and hydrogen peroxide, with which it exists in equilibrium, are toxic to fish. Lethal concentration doses are of the same order of magnitude to those used in practice, although residuals would be expected to be low. There is also considerable concern over the mutagenic properties of all three of the equilibrium components of the peroxygen disinfectant: PAA, hydrogen peroxide and acetic acid. The possible formation of harmful by-products such as epoxides and the generation of chlorine from seawater, by a free radical mechanism, requires further research.

4 Although the capital costs are low, the high costs of the chemical results in a total cost of approximately five times that of chlorine.

8 BROMINE CHLORIDE

8.1 Introduction

Bromine chloride is an interhalogen compound with properties intermediate between those of chlorine and bromine. Below 5°C it is a fuming, corrosive liquid which requires extreme care in metering and handling. Interest in the use of bromine chloride as a wastewater disinfectant was first shown the the mid 1970's and several pilot studies were conducted. However, it still remains in the experimental stage and no operational full scale wastewater plants are known to date. Despite a number of advantages over chlorine, including a greater virucidal efficiency and lower residual toxicity, the reliability of storage and dispensing methods has been a major restriction in its widespread application.

8.2 Production and application

Bromine chloride is an equilibrium mixture of bromine and chlorine which exists as a dark red liquid at < 5°C, 1 atm. It is a hazardous, corrosive chemical, irritating to the eyes and respiratory tract at even low concentrations of the vapour. In general, its properties are intermediate between either bromine or chlorine with the exception that it is eleven times more soluble than chlorine.

It is prepared by the addition of gaseous or liquid chlorine to an equivalent amount of bromine until the mixture increases in weight by 44.3% (White, 1986). Alternatively it may be produced by the reaction of bromine in an aqueous hydrochloric acid solution. Bromine chloride is supplied as a liquid in 68 kg cylinders or 1365 kg containers (EPA, 1986). The greater density of bromine chloride compared to chlorine permits a given container to hold 50% more bromine chloride. The much lower vapour pressures means that accidental leaks can be more easily contained.

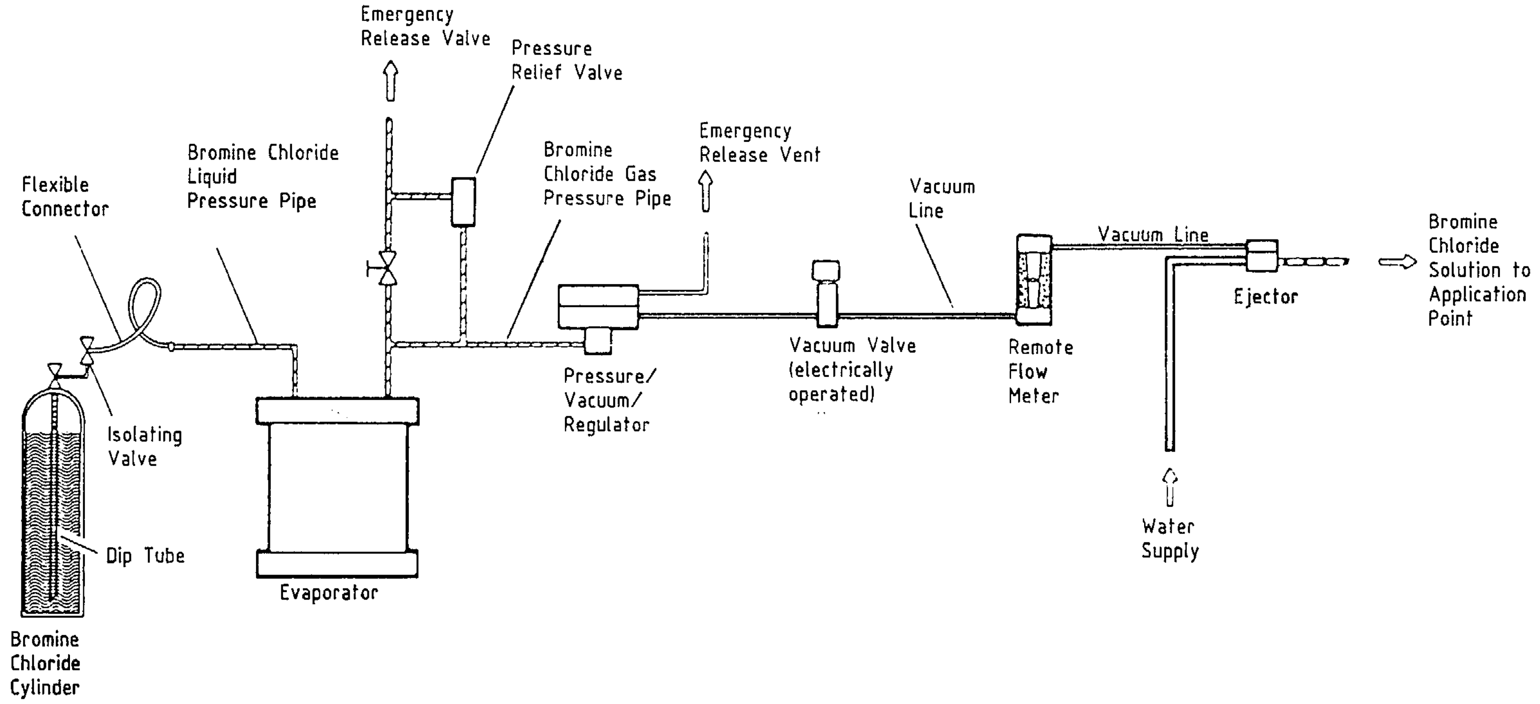


Fig 8.1 Bromine chloride metering and control equipment (White, 1986)

Bromine chloride is applied either in gaseous form or in aqueous stock solutions. To prevent chemical dissociation and enrichment of gaseous chlorine, liquid rather than gaseous withdrawal is necessary, with external evaporation. Bromochlorinators and solution ejectors analogous to those used in chlorine systems may be used. Since the vapour phase is relatively enriched with chlorine, bromine chloride has to be withdrawn from the liquid phase by a dipstick. It is then transferred by pressure from the supply cylinder into a vaporiser where it is superheated to prevent reliquification. The bromine chloride pressure is then reduced, and the gas is metered and directed to the ejector which mixes it with the process water stream.

Operational difficulties which have occured at pilot plants have been due to higher levels of impurities in bromine chloride compared to chlorine. These have caused clogging of evaporators and led to some manufacturers testing the possibility of direct liquid dosing (EPA, 1986). In pilot studies with bromine chloride (LeBlanc and McEuen, 1978) the solids clogging the evaporator were found to be a combination of Br^- and Cl^- salts of iron. The use of nickel in the evaporator, whilst adding to the process costs, should prevent this.

8.3 Mechanism of Inactivation

From the limited work on the mechanism of bromine chloride inactivation, it is thought that viral disinfection proceeds via disruption of the protein capsid. The similarity in the rate of bacterial inactivation with that of chlorine suggests that the mechanism may also be similar, though this has yet to be confirmed.

The mechanism of inactivation of poliovirus using bromine chloride was investigated by Keswick (1981) by correlating the loss of viral infectivity with structural changes. It was found that a bromine chloride dose of 0.3 - 5 mgl^{-1} led to 95 - 100% inactivation, but the inactivated virus retained its structural integrity. A dose of

10 - 20 mgl^{-1} however, led to total inactivation, associated with the degradation of virus structural integrity. It was concluded that bromine chloride as HOBr or bromamines inactivates poliovirus by reacting with the protein coat whilst the RNA is neither inactivated nor released.

In work conducted by Taylor (1982) bromine chloride was found to inactivate bacteriophage f_2 without preventing specific adsorption; at higher doses adsorption was lost as well as infectivity, suggesting that damage to the capsid had occurred.

8.4 Disinfection efficiency

Though chlorine and bromine chloride are equally effective as bactericides, it appears bromine chloride is a more efficient virucide, particularly in the presence of organic or inorganic interfering substances.

In a study to evaluate the efficiency of bromine chloride as an alternative to chlorine by Keswick *et al* (1980), activated sludge effluent was treated with various doses of bromine chloride and chlorine for 15 min at 25°C. Whilst 8 mgl^{-1} bromine chloride or chlorine reduced the coliform concentration by 4 - 5 log, bromine chloride was found to be more effective than chlorine in inactivating seeded enteric viruses, giving greater than 4 log reductions of coxsackie B4, echo-7, Reo-2 and Polio-I virus. In contrast, the same dose of chlorine gave a 1.7 - 3.8 log reduction of virus. To evaluate efficacy in disinfection of natural pathogen populations in effluent, experiments were conducted under field operating conditions. Again bromine chloride proved more efficient as a virucide, reducing viruses to undetectable levels whereas in effluent treated with chlorine, viruses were still detectable.

8.5 Toxicity and by-product formation

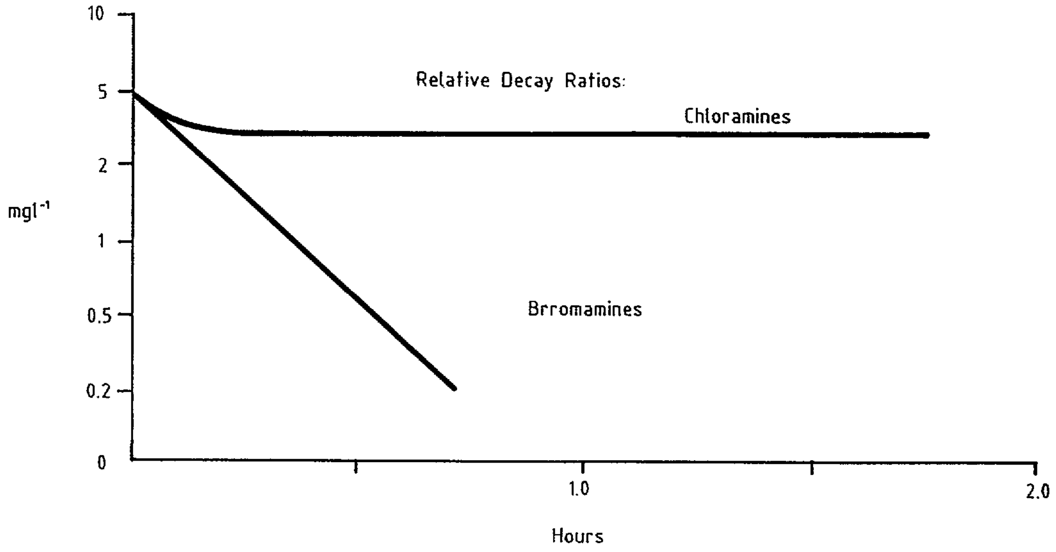
In water, bromine chloride hydrolyses almost exclusively to hypobromous and hypochlorous acids. The hypobromous acid subsequently dissociates and reacts with nitrogenous compounds to form bromamines, in an analogous way to hypochlorous acid. In wastewater, the formation of bromamines is probably much faster than the formation of chloramines.

Bromamines are shortlived. Measurements of residual decay found the half-life of bromine chloride residuals in secondary effluents to be less than 10 min compared to those of around 20 for the corresponding chloramines (LeBlanc and McEuen, 1978). It was found that the application of chlorine resulted in the formation of a stable residual after the first minute when the initial demand had been satisfied. By contrast, the bromine chloride formed unstable residuals which decayed rapidly with a 70 - 100% reduction in residual after 30 min to ≤ 0.02 mgl^{-1}, compared to 1.0 - 2.0 mgl^{-1} for chlorine.

It is likely that the higher decay rates of residual bromine chloride result in disinfected effluents of a lower toxicity. In a 96h fish survival test, fathead minnows were immersed in diluted effluents treated with equal dosages of chlorine and bromine chloride. The chlorinated effluent killed all fish in 20 min while that treated with bromine chloride caused zero kill (Greene, 1981).

Acute toxicity tests conducted with chlorobrominated wastewater effluent in pilot trials at Grandville, Michigan (Ward *et al*, 1976) indicated that bromine chloride residuals were not as lethal as chlorine. In contrast, later work at Wyoming involving wastewater with a large non-domestic component, treated by trickling filter (Ward and De Graeve, 1980), showed that most fish exposed to bromine chloride disinfected effluent exhibited mortality patterns and stress symptoms similar to those tested in the chlorinated effluent. Exceptions were salmonids, which were more sensitive to bromine chloride than chlorine. Little mortality was recorded with macroinvertebrates. The difference between toxic effects at Grandville and Wyoming may have been due to synergistic or additive action involving bromine chloride and some other

Fig 8.2 Relative decay ratios of bromamines and chloramines in wastewater (Greene, 1981)



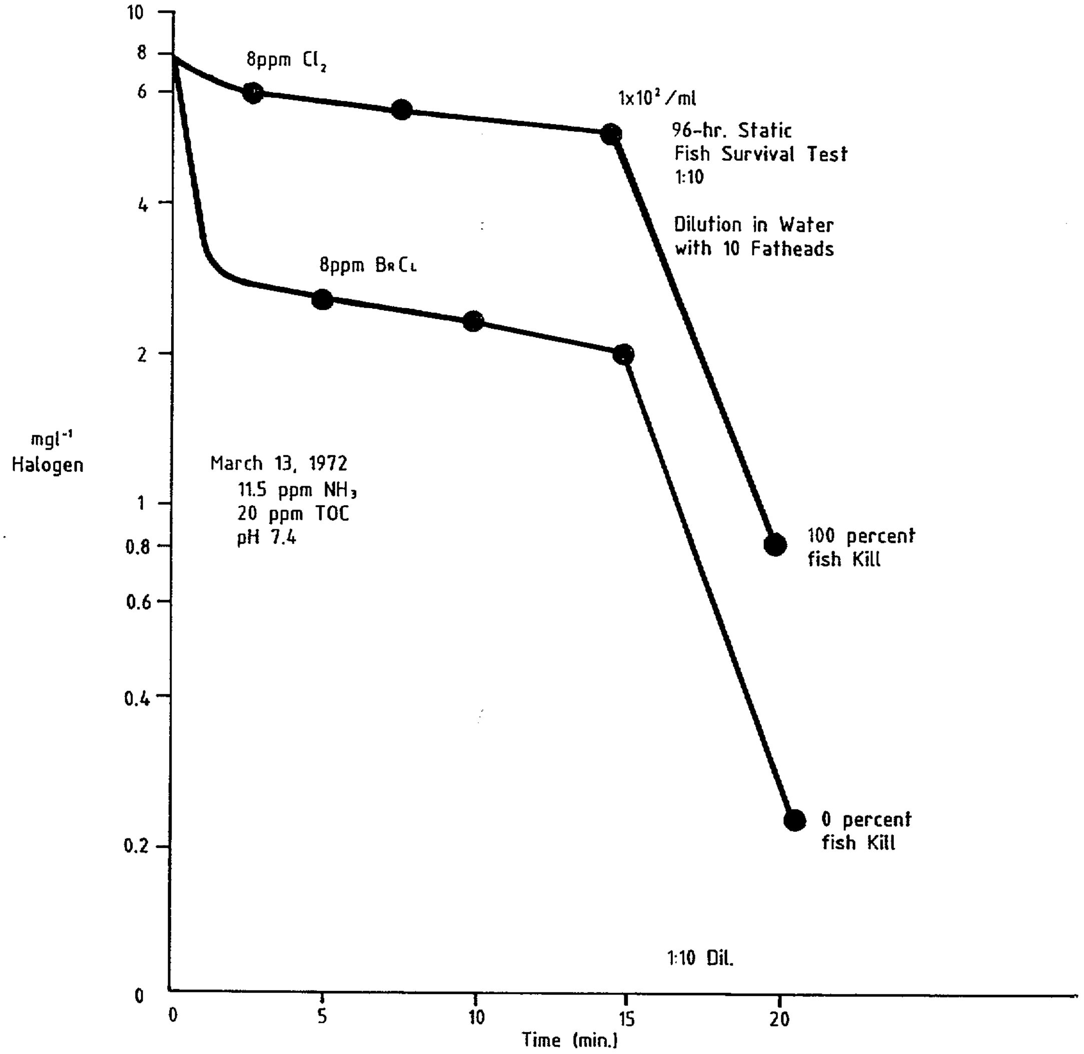


Fig 8.3 Results of a 96h fish survival test conducted with equal dosages of chlorine and bromine chloride in diluted secondary effluent (Greene,1981)

component (possibly cyanide).

The effects of disinfected condenser-cooling effluents on selected estuarine species (fish, bivalves and invertebrates) appeared to be similar for both bromine chloride and chlorine (Liden *et al*, 1980). Bromine chloride appeared to be less toxic to zooplankton than equivalent concentrations of chlorine.

In wastewater, bromine chloride and its hydrolysis products react rapidly with ammonia to form bromamines with mostly dibromamine at the pH range normally encountered. Brominated species are much better oxidants than the analogous chlorine compounds, which tend to be more efficient at halogenation. The C-Br bond is less stable than C-Cl and it is possible that reductive degradation through debromination may occur. In general, compounds which are more readily brominated are also more susceptible to degradation by hydrolysis or photochemical pathways, which reduces the incidence of brominated organic compound formation.

However there is a possibility that disinfection with bromine chloride will lead to an increase in brominated THMs, which may pose more serious problems than the chlorinated analogues. Studies have indicated that when bromide is present in waters receiving chlorinated effluents there is an increase in THMs (Cooper *et al*, 1985). The incorporation of bromine into higher molecular weight organics and their possible mutagenic or carcinogenic properties remains to be investigated. It has been shown that brominated organics accumulate in fish exposed to effluents disinfected with bromine chloride (WPCF, 1987). Bromoform ($CHBr_3$) is the major organic product of bromination, but other less volatile and hence longer lasting products such as tribromophenol and tribromoanisole have also been identified as products of wastewater bromination (WPCF, 1986). The presence of certain organic nitrogen compounds may also lead to the persistance of a total bromine residual for several hours (White, 1986).

8.6 Costs

Bromine chloride has two cost advantages over chlorine - firstly because of its higher density, greater volumes may be shipped in smaller containers. Secondly, because of the generally lower contact time required for disinfection, smaller contact chambers may be used, or more effluent treated in an existing contact chamber. From the work by Leblanc and McEuen(1978), the residual decay curves of bromine chloride indicate that most disinfection may occur in the first 15 min of contact, in which case capital costs may be decreased by the use of a lower contact time.

Trials conducted at an activated sluge secondary wastewater treatment plant in Maryland demonstrated that bromine chloride is cost competitive over chlorination/dechlorination and ozonation (Table 8.1). A comparison of capital and operating costs for a range of disinfection processes and plant sizes operating on secondary effluent also showed that bromine chlorine costs were comparable with chlorination/dechlorination and some 10 - 40% higher than chlorine alone (Rivoal, 1983).

8.7 Conclusions

1. Whilst chlorine and bromine chloride appear equally effective as bactericides, bromine chloride would appear to inactivate enteric viruses more efficiently, in the presence or absence of interfering organic substances.

2. The half-life of residuals are much shorter than the analogous chlorine compounds, giving a lower residual toxicity. Trials on bromine-chlorinated wastewaters have proved that they have similar or lower toxicity than chlorinated effluent. However the presence of Br^- facilitates formation of THMs and brominated THMs.

3. Bromine chloride is a noxious hazardous compound requiring particular care in handling. In addition there is a tendency for it to reliquify with the dissociation of vapour.

4. Though bromine chloride is more costly than chlorine, the higher density and reactivity means smaller contact chambers may be used, with resultant lower capital costs.

Table 8.1: Total treatment costs (pm^{-3})* of bromine chloride compared to other disinfectants for a range of plant sizes (Greene, 1981)

Disinfection Alternative	Plant Size (m^{3}d^{-1})		
	3,800	38,000	380,000
Chlorination (8 mgl^{-1})	0.7	0.3	0.2
Chlorination/Dechlorination with SO_2 (2.5 mgl^{-1})	1.0	0.4	0.2
Chlorination/Dechlorination with SO_2 - Post Aeration	1.4	0.6	0.3
Ozonation (Air) (10 mgl^{-1})	2.2	1.3	1.0
Ozonation (Oxygen) (10 mgl^{-1})	2.0	1.0	0.7
Chlorobromination (BrCl) (5 mgl^{-1})	1.2	0.5	0.2

* conversion of 1980 US$ value at 1988 exchange rate of 1 US$ = £0.57

9 RADIATION

9.1 Introduction

Application of wastewater irradiation is limited primarily because of cost but it has been studied as a means of disinfecting sludge prior to land application in a number of countries. Pilot trials have been conducted in USA, Canada and the USSR on wastewater and on sludge in Germany. Energised particles are already used medically for cancer therapy; industrially for cross-linking of polymeric materials and in the irradiation of food to increase the shelf life of grains and fruits. The treatment of sewage effluents would require radiation doses of a similar magnitude to those applied in food irradiation.

The costs of treatment are high, mainly due to the high capital costs of the handling and shielding equipment and the costs of replenishing the source. Safety considerations to personnel and prevention of the leakage of radioactive material through corrosion are of paramount importance. The potential effects of irradiation on the nature of the sewage matrix and of the discharge of irradiated effluents to the marine environment are as yet unknown.

9.2 Production and application

Commercially, radiation energy can be produced from either an electron accelerator or a gamma-radiation source such as Cobalt-60 or Caesium-137.

9.2.1 Electron Acceleration

High voltage accelerators, energising electrons in vacuum by a few million volts are capable of producing intense beams of very high energy electrons at a rate of typically 10^{12} radh^{-1} which is 10^6-10^7 times faster than gamma-radiation. Commercial accelerators are limited to voltages below 15MV but most are in the range 0.5-3.0 MV; with power outputs of approximately 100kW (Ballantine 1978). A 2 MV electron beam carrying 100kW of ionising power injects 3 x 10^{17} electrons per second, each electron producing about 60,000 ionising collisions before being de-energised to its normal state (Trump *et al*, 1984). A serious limitation of energised electrons is their relatively short penetration range, unlike gamma rays which are deeply penetrating (Ballantine, 1978).

9.2.2 Gamma Radiation

Gamma-radiation is emitted from radioisotopes such as Co-60 or Cs-137. Co-60 is produced by deliberate exposure of natural cobalt to neutrons in nuclear reactors and emits two high energy gamma-rays of 1.17 and 1.33 MeV. Cs-137 is a major by-product of nuclear fission and may be separated from a mixture of fission products. Only one photon of gamma-radiation is released per disintegration compared to two for Co-60, and the energy per photon is half that of Co-60, so that the efficiency as a disinfectant is lower on a per curie basis. The maximum useful dose rate from Co-60 and Cs-137 is approximately 1 Mrad h^{-1} (10^6 $radh^{-1}$).

9.2.3 Safety aspects

Energised electrons are widely used in industry for such applications as cross linking of wire and cable, modification of textiles and various plastics. There is also considerable experience with the use of gamma-radiation sources with more than 36 Co-60 plants in operation. There are no moving parts involved and the rate of energy release is ruled by the laws of radioactive decay. However, radiation is inherently hazardous and proper protection and shielding facilities are vital so that average daily operator exposure to radiation conforms to international limits. Irradiators must be shielded by concrete housing and earthworks and access of personnel carefully controlled. Leakage of radioactive material through corrosion has to be prevented as Cs-137 occurs in the form of a highly water-soluble chloride which can cause problems (Ballantine, 1978).

Limits for radionuclides in drinking water are being considered by the US EPA. In 1989 maximum contaminant level goals (MCLGS) for radon, radium, uranium, gross-gamma, gross beta and photon emitters will be specified.

9.3 Mechanism of inactivation

Though both radiation and UV act upon the nucleic acids of the microorganisms, the mechanism of attack is fundamentally different. In 1963, Wacker proposed that x rays destroy nucleic acids both directly and indirectly. Inactivation due to a direct hit of a portion of radiation energy is due to splitting of the bases, the sugar and the phosphate bridge bond in the RNA. The Sandia reports 1975-1981 extensively studied the interaction of viruses and ionising irradiation and found that the inactivation of poliovirus was primarily due to RNA damage though damage to the capsid may have a contributory effect. RNA damage was thought to be caused mainly by base rather than strand damage (Epp, 1982).

The indirect impact of ionising radiation is caused by the effect of the radical products of the radiolysis of water such as HO_2, OH radicals, peroxides and hydrated electrons. The studies on poliovirus showed very little inactivation of RNA but damage to the capsid was indicated by the loss of cell adsorption ability. The cell capsid damage in viruses has also been confirmed by Ballantine (1978) and Dolin and Brusentseva (1981).

The indirect mechanism of inactivation is being utilised for the chemical oxidation of organic pollutants in the USSR and China. The radical chemical oxidation method is being developed for treatment of natural waters with a high humic content though it is difficult to achieve a chain reaction and is therefore only suitable when relatively small doses are required.

9.4 Disinfection efficiency

Table 9.1 indicates the D_{10} doses (electron dose for 90% inactivation) for inactivation of a variety of microorganisms in pure cultures. As with other disinfectants, coliforms are less resistant than viruses which are less resistant than bacterial spores, with electron doses ranging from 10-200 krad for 90% kill.

Pilot studies conducted on a range of wastewaters have shown that adequate reductions of microorganisms can be achieved with doses of 100-400 krad (Table 9.2). Survival dose studies on pure cultures and on raw and anaerobically digested primary sludges showed that a 400 krad dose (which raises the temperature of the effluent by 1°C) achieved substantial reductions in pathogenic bacteria of 4-5 logs and in human enteric viruses of 1-2 logs (Trump *et al*, 1982). This is adequate for anaerobically digested sludge though higher doses would probably be required for raw sludge. Domestic wastewater requires a 50 krad dose for adequate disinfection.

Disinfection efficiency is enhanced by high temperatures and extremes of pH (3 and 10-11) whereas aggregation and adsorption of microorganisms to particles adversely affects inactivation efficiency.

9.5 Pilot studies

There have been a number of studies in the use of radiation for disinfection; the most comprehensive studies have been made in the USSR and USA. The use of irradiation for sludge disinfection has been investigated at Munich, Germany where a Co-60 source is used to irradiate up to 150 m^3d^{-1} of municipal sludge, at a 300 krad dose, prior to its application on pasture land (Ballantine, 1978).

Table 9.1: D_{10} (90 percent) inactivation electron dose for various microorganisms in pure cultures (Trump et al, 1982)

	D_{10}Dose (krads)	Calculated Log_{10} Reduction for 400 Kilorad Electron Dose
Escherichia coli strain K12	27	15.0
Microoccus species	14	28.0
Citrobacter freundil	5	80.0
Klebsiella pneumoniae	12	33.3
Salmonella enteritidis	15	26.6
Salmonella typhimurium strain LT2	16	25.0
Salmonella typhimurium strain R6008	105	3.8
Salmonella typhimurium strain 24	30	13.0
Streptococcus faecalis	125	3.2
Clostridium perfringenes spores strain 8798	200	2.0
Clostridium perfringenes vegetative cells strain 8798	75	5.3
Aspergillus niger spores	31	13.0
Poliovirus type 2	185	2.2
Coxsackievirus type B3	200	2.0
Echovirus type 7	170	2.3
Reovirus type 1	165	2.4
Adenovirus type 5	150	2.6
Bacteriophage P22	60	6.6

Table 9.2: Summary of reported disinfection efficiencies for irradiation.

Medium	Dose (krad)	Inactivation efficiency	Reference
Pure culture	100	2 log: 10 organisms	Ballantine (1978)
Sewage	>100		
Settled sewage	100	4 log: total bacteria	
Settled sewage	4000	100% kill	
Settled sewage	150	4 log: coliforms 95% kill: faecal streptococci	
	250	100% kill: *E.coli*, enteroccocus, coliphage 92% kill: spores	Pikaev and Shubin (1984)
Liquid sludge	400	disinfection	Trump *et al* (1982)
Municipal wastewater	50		
livestock complex wastewater	200	100% kill	Dolin and Brusentseva (1981)
Domestic sewage	50	100% kill	
secondary effluent	100	4 log	Shubin *et al* (1984)

At Boston, Massachusetts, a six year pilot study started in 1974 investigated the use of energised electrons for disinfection of mainly liquid sludge and wastewater (Trump, 1984; Cleland *et al*, 1984). Demonstration facilities were built at Deer Island, Massachusetts, to evaluate the biological, chemical and physical effects of radiation. At the pilot plant, a carefully shaped liquid stream was caused to flow through an intensely ionising electron beam which swept repeatedly across the stream width and penetrated its full thickness. A 50kW, 750 kV electron accelerator was found to be capable of treating up to 3785 m^3d^{-1} sludge at a dose of 400 krad. The treatment of wastewater rather than sludge allowed for higher flow rates and led towards electron injection from opposite sides to permit doubling of the thickness of the wastestream and to increase the electron utilisation efficiency (see Figure 9.1).

A study to evaluate the technical and economic feasibility of various methods for disinfecting wastewater in the Canadian Arctic, with specific reference to gamma-radiation, estimated environmental impact and costs for all technically feasible disinfection processes (Canada Mortgage and Housing Corporation, 1981). It was stated that gamma-irradiation was not expected to have any significant environmental impact. The production of radioactive by-products was thought highly unlikely because the disintegration energy of Co-60 is low relative to other elements and only one or two uncommon elements would be susceptible to neutron displacement by radiation from Co-60. However, the effects of radiation on water quality were relatively unknown and the impact of the construction of a radiation facility was thought to be significant. There was little evidence to suggest any increase in virulence would result from disinfection with radiation, although work conducted at the Sandia laboratories reported that at dosages necessary for disinfection, the probability of mutation is very high. However, resultant strains generally have multiple mutations, are difficult to grow under ideal conditions and would not survive in normal conditions.

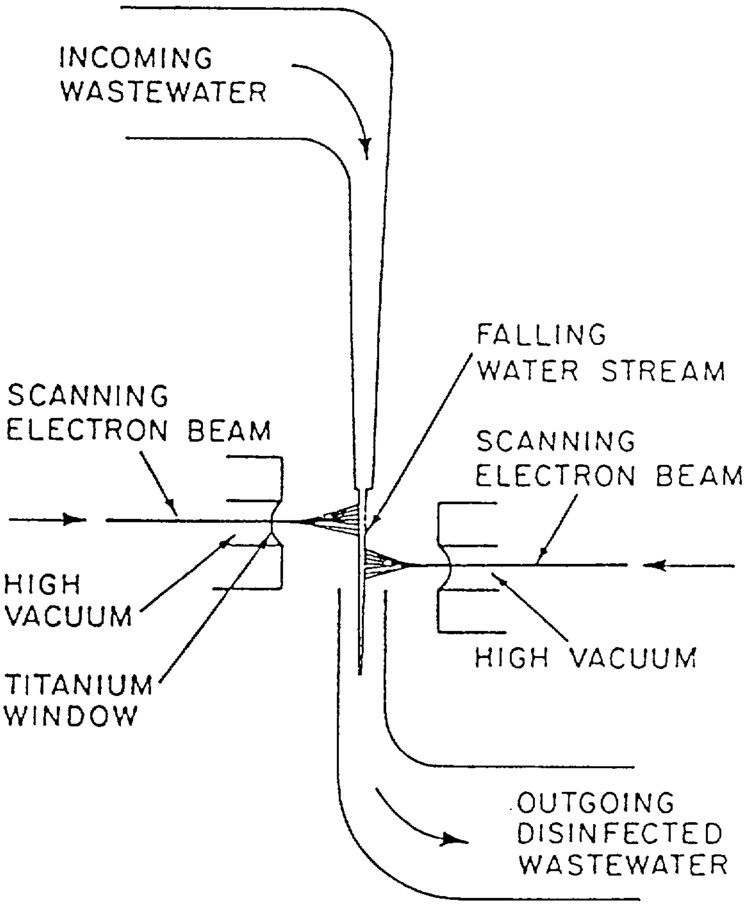


Fig 9.1 Dual-beam process proposed for wastewater disinfection by accelerated electron radiation (Cleland et al, 1984)

Other pilot facilities in the USSR have studied the use of accelerated electrons for the disinfection of wastewater from livestock complexes (Dolin and Brusentseva, 1981). A 9 MeV accelerator, and a dose of 200 krad was found to give 100% disinfection of pathogenic bacteria and helminth embryos.

At a 38 m^3d^{-1} commercial plant in the US, a 16000Ci Co-60 source is used to treat secondary effluent. A dose of 50 krad led to a log 4 reduction in coliforms and 100% reduction in influenza and polioviruses. In addition there was an improvement in chemical, physical and biological parameters (Dolin and Brusentseva, 1981; Pikaev and Shubin, 1984).

9.6 Costs

An economic comparison of sludge disinfection using different radiation sources for a 378m^3d^{-1} sludge output and dose of 200 krad was conducted at the Deer Island facility by Ballantine (1978). This led to a theoretical radiation requirement of 13 kW. The estimated capital and operating costs for a 3MV accelerator, a Co-60 source and a Cs-137 source are shown in Table 9.3. The capital cost for the source was substantially lower for the electron accelerator whilst handling and shielding costs were fixed for all three radiation sources and represented more than half the initial capital costs or less than a sixth depending on the source.

The largest single part of capital costs for gamma-irradiation is the initial purchase of a gamma-source. Similarly, the annual purchase of replacement rods is the most costly item in operating costs (Canada Mortgage and Housing Corporation, 1981) such that total costs for the gamma sources are roughly double those of the electron accelerator. These costs will be substantially lower for wastewater disinfection which requires a dosage of perhaps 50 krad; thus reducing both the initial capital costs and the

Table 9.3: Comparison of costs for a sludge irradiation plant based on a dose of 200 krad, 378 m^3d^{-1} liquid sludge output (Ballantine, 1978)

	^{60}Co	^{137}Cs	3 MV accelerator
Source	650,000	970,000	100,000
Shielding/handling	150,000	150,000	150,000
Initial capital	800,000	1120,000	250,000
Amortisation (20 y)	40,00	56,000	12,500
Source replenishment and maintenance	81,250	22,300	10,000
Interest	40,000	56,000	12,500
Labour	20,000	20,000	40,000
Power @ \$0.02 kwh^{-1}	-	-	7,000
Total	181,250	154,300	82,000
Cost (\$$m^{-3}$)	0. 89	0. 75	0. 40
(pm^{-3})*	50	43	23

* Conversion of 1978 US\$ at a 1988 exchange rate of 1US\$=£0.57

subsequent source replacement costs by an order of magnitude.

Measurements made at the Deer Island facility (Cleland *et al*, 1984) have shown that municipal wastewater can be adequately disinfected with a 50 krad dose. This low dose requirement would lead to an increase in throughput of an order of magnitude and operating costs would be reduced accordingly. A dosage of 50 krad for a flow of 23000 m^3d^{-1} could be maintained by two 100 kW, 2MV electron accelerators. The cost for a dual-beam facility was estimated at \$2.5 million (£1.4 million) and total treatment costs would be $9cm^{-3}$ $(5pm^{-3})$.

Gamma ray disinfection tends to be less expensive than electron treatment for small facilities requiring less than 10 kW of emitted power; the cost of gamma-sources being proportional to their capacity. The voltage rating is the main determinant of the cost of an accelerator rather than the beam current or power rating (Cleland *et al*, 1984). The capital cost of Cs-137 sources is about the same as Co-60 for the equivalent emitted power. However the intrinsic gamma-emission is much lower for Cs-137 and reduces the emitted power accordingly. The replenishment cost of Cs-137 is lower than Co-60 because of its longer half-life, thus the cost per unit volume is much lower.

In a study in which the economic feasibility of various disinfection alternatives was evaluated, the capital and operating costs for chlorination, chlorination/dechlorination, ozone, UV, lime and gamma irradiation were estimated for weak sewage and lagoon effluent. The capital costs of chlorine, chlorine/dechlorination and UV were approximately similar and roughly an order of magnitude lower than capital costs for gamma-radiation and lime. Ozone capital costs were approximately double those of the chlorine alternatives. The operating costs followed a similar pattern to the capital costs.

9.8 Conclusions

1 Ionising irradiation is an effective disinfection treatment process for a wide range of microorganisms. It is also suitable for sludge disinfection due to its highly penetrating nature.

2 Although widely used for industrial applications there is little experience in the disinfection of wastewater. Considerable attention must be given to proper protection and shielding facilities to minimise both the real and perceived risk to operating personnel and the general public.

3 There has been insufficient work done on the effects of radiation on wastewater quality for a quantitative assessment of the environmental hazards. The construction of a radiation facility is likely to have a significant environmental impact.

4 Radiation methods are a costly means of disinfection; total treatment costs are an order of magnitude higher than the conventional alternatives. Gamma radiation sources tend to be less expensive than electron treatment for small facilities, but the latter show economies of scale.

Possible Disinfection Techniques

10. POSSIBLE DISINFECTION TECHNIQUES

10.1 Bromine

Bromine is considered to be the most reactive oxidant of all the halogens (except fluorine). It is a dark brownish-red liquid with a penetrating heavy odour and is both difficult and hazardous to handle. It exists primarily in the bromide form (in seawater, brine and salt deposits) and commercial production is mainly by chemical oxidation. To minimise hazards it may be handled in the solid form; anion exchange resins also release bromine from the polybromide form - marketed as disposable cartridge type brominators (Grabow, 1982). Its major application is as a swimming pool disinfectant.

Bromine resembles chlorine with respect to hydrolysis; dissociating in water to give hypobromous acid (HOBr) and the hypobromite ion (OBr^-), the species distribution depending on pH. These react with ammonia to form bromamines. Unlike chlorine, the hypobromite ion may be more effective as a disinfectant than hypobromous acid, but bromamines are less efficient. However the species which would predominate in wastewater disinfection, dibromoamine ($NHBr_2$) has germicidal properties almost equivalent to free chlorine (White, 1986) therefore inactivation efficiency at elevated pH is likely to be higher than for chlorine.

Though all bromine species are more effective oxidising agents than the analogous chlorine species (and thus less efficient as halogenating agents), much is utilised in satisfying the halogen demand, so that whereas 8 mgl^{-1} chlorine will achieve disinfection, 45 mgl^{-1} bromine is required. The combination of prechlorination to satisfy oxidant demand, followed by bromination will thus achieve superior disinfection. This was demonstrated in pilot studies (Fressonnet-Chambarlhac *et al*, 1983a) on secondary effluent in which a smaller dose range for inactivation of coliforms, enteroviruses and coliphages was required for prechlorination and bromination than chlorine alone.

Jurion *et al* (1982) conducted a pilot study on the disinfection of wastewater to establish bactericidal efficiency of bromine and its effect on physico-chemical parameters. Optimal bromine disinfection secondary effluent was found to occur after 6 min contact time; a residual concentration of 0.03 - 0.85 mgl^{-1} achieved a 2.5 - 4 log reduction in faecal coliforms and faecal streptococci.

Whilst bromine residuals are much shorter lived than the analogous chlorine compounds, the reduction of bromamines by organics and the subsequent formation of undesirable bromoorganics is a potential hazard. The end product of bromination, the bromide ion (Br^-) also facilitates the formation of brominated THMs. Much less is known about brominated THMs than chloroform, and it is possible that toxicological effects of brominated compounds may exceed those of chloroform (Cooper *et al*, 1985).

The high costs of bromine make it prohibitive for wastewater treatment unless a prechlorination stage is employed. The hazards associated with its handling (which incidentally led to the development of bromine chloride as a safer alternative) and the unquantified environmental risks also mitigate against its use.

10.2 Heat

In the sewage disposal field, heat has been used for the pasteurisation of sewage sludge, usually at 70°C for 30 min. It is highly effective for reducing numbers of enteric bacteria, including *Salmonella*. Pilot and full scale plants operating in Switzerland and Germany have demonstrated that prepasteurisation followed by anaerobic digestion produces a stable sludge in which regrowth of *Salmonella* and other bacteria does not occur (Havelaar, 1983). A prepasteurisation plant for sewage sludge is operating at the Colbourn Works, Yorkshire Water.

Heat applied to sewage would also be expected to give substantial reductions in microorganisms, but may not however, kill all pathogens. A temperature of 70°C for 30 min has been shown to inactivate poliovirus and hepatitis A virus (Flehmig *et al*, 1985) but some other viruses can survive boiling for 2-3 min. Heating to 100°C for 30 min on three successive days is necessary to kill bacterial spores, which germinate in the periods between heating cycles.

Experiments on heat disinfection of crude and treated sewage using microwave irradiation (Sanborn and Keyser, 1982) demonstrated significant bacterial and viral activity at 50°C and some bacterial activity at 85°C. Boiling, however, inactivated bacteria and viruses (poliovirus type 1, parainfluenza I and T4 phage) in both raw sewage and treated effluent (Table 10.1).

Stramer and Cliver (1984) concluded that heat (55°C) and peroxide was an effective disinfection system for sewage, but that the combination was not practical for on-site use. Although obviously an efficient inactivation method, economic considerations effectively exclude heat as a competitive disinfection method.

10.3 Sensitized photo-oxidation

The use of sunlight and photosensitizers such as methylene blue has been proposed for wastewater disinfection. The sensitizer absorbs solar energy in the visible spectral region and transfers the energy either to organic matter or to molecular oxygen. Unsaturated compounds are oxidised to peroxides which subsequently generate free radical oxidation reactions. The cellular constituents of target microorganisms are altered and reproduction is inhibited as a result. Reported inactivation efficiencies in wastewater effluents range from 2-4 log for coliforms at an exposure time of 2h (Marzouk *et al*, 1982; Eisenberg *et al*, 1987); 4 log (3h) for enterococci; 3 log (4-8h) for poliovirus type 1; and 4 log (1h) for coliphage f2 (Marzouk *et al*, 1982). Turbidity reduced total bacteria and coliform removal to 1-2 log.

Table 10.1 Heat inactivation of virus and bacteria in 1000 ml volumes of wastewater by microwave irradiation (Sanborn and Keyser, 1982).

Microwave Time[1]	0	3	6	9	12
Sample Temperature	23	50	70	85	Boiling
Raw Sewage					
bacterial activity	+[3]	+	+	+	-
viral activity	+	+	-	-	-
Filtered Raw Sewage[2]					
bacterial activity	+	+	-	-	-
viral activity	+	+	-	-	-
Treatment Plant Effluent Sewage					
bacterial activity	+	+	+	+	-
viral activity	+	+	-	-	-
Filtered Treatment Plant Effluent Sewage[2]					
bacterial activity	-	-	-	-	-
viral activity	+	+	-	-	-

[1] Microwave time in minutes; temperature in °C

[2] Exogenous virus added

[3] +indicates presence of bacteria or virus
-indicates absence of bacteria or virus

Advantages of the system are the low-cost energy source, the self-regeneration of the photosensitizer, the short contact times required and the lack of toxic by-products in comparison to chlorine. Even though disinfection may only be required in summer, the sunlight intensity in the UK would be too low and inconsistent for its application. Turbidity effects also suggest that it would be unsuitable for crude sewage, while problems could arise with land requirements for lagoons, and aspects of public acceptability.

10.4 Quarternary ammonium compounds

Quarternary ammonium compounds in solution are known to be highly effective bactericides. Whilst highly effective against lipid-containing enveloped viruses (eg. influenza) they are not as effective for non lipid-containing viruses (eg. enteroviruses) and require high concentrations and high pH values of >10.5 (Gerba *et al*, 1984).

A number of chemical disinfectants were tested by Lloyd-Evans *et al* (1986) for their ability to disinfect against human rotavirus. Quarternary ammonium compounds were found to be effective in combination with:

a) alcohols at >40%
b) some acids eg. hydrochloric acid
c) some bases eg. sodium metasilicate.

To avoid the problem of residual disinfectant toxicity, Gerba *et al* (1984) developed an insoluble polymeric contact disinfectant (IPCD) by permanent immobilisation of quarternary ammonium compounds onto a commercial chloromethylated crosslinked polystyrene resin. This produced a high concentration of functional disinfectant at the surface of the resin, where microorganisms could be absorbed and inactivated.

In flow through column and batch studies, IPCD was shown to give highly efficient removal and inactivation of *E.coli* and *Bacillus subtilis*. A volume of 2.3 l of water containing 9.4 x 10^8 bacterial cells could be passed through 1 g of resin before any breakthrough was observed (Janauer *et al*, 1981). Removals of 99.9% were observed for poliovirous type 1 and simian rotavirus SA-11 after passage of 1500 ml of water containing 10^4 PFU ml^{-1} of virus through a 1 ml bed of resin (Gerba *et al*, 1984).

Advantages of this system are that the resin can be regenerated, is active in the presence of organic matter and does not release the disinfectant into the treatment stream. It may have applications for point-of-use drinking water systems and small water treatment facilities. In terms of wastewater disinfection however, column applications would be limited by solids clogging. With a suitable separation facility, batch treatment could be feasible, but the efficacy of a non-penetrative disinfectant on encapsulated organisms would be questionable. Inefficiency with regard to inactivation of enteroviruses also detracts from its further development.

10.5 Activated carbon adsorption

Activated carbon has been considered as a tertiary treatment for sewage effluent for the removal of viruses. Poliovirus removals of 18-40% (Sproul *et al*, 1969) and 24-50% (Gerba *et al*, 1975) have been reported for secondary effluents. Adsorption of virus is pH dependent, peaking at < pH 4.5. This value corresponds to the lower isoeletric point for poliovirus; the positive electric charge on the virion enhancing its electrostatic attraction onto the negatively charged groups of the activated carbon.

Although useful as an incidental process during final polishing of treated effluents, viral removal with activated carbon would not appear to be a cost-effective or efficient option for wastewater.

The minimal viral adsorption observed at the natural pH of sewage (7.5-8.5) combined with competitive adsorption of organic material (Gerba *et al*, 1975) and the high cost of activated carbon mitigate against its use.

10.6 Protein precipitants

Protein precipitants such as phenol (Lysol), formaldehyde, alcohols, detergents, acids and alkalis are frequently used as sterilants. They act by denaturing viral proteins. Although effective for laboratory or clinical applications, protein precipitants used in a sewage matrix would be anticipated to provide a protective rather than destructive role. The high concentrations of proteinaceous material in wastewaters would precipitate around the indigenous microorganisms, forming a protective coating around viable cells or virus particles.

This effect is demonstrated by the practice of adding protein in the form of BSA or serum to samples of virus to enhance their survival between removal from the host and subsequent assay. Cell aggregation and encapsulation by wastewater solids forms one of the most significant barriers to efficient disinfection, thus any agent which enhances this effect will be of little benefit.

Use of acids such as hydrochloric, sulphuric and phosphoric at high concentrations in disinfectant formulations has been found to give a greater than 3 log reduction in rotavirus suspensions (Springthorpe *et al*, 1986). However, enteroviruses may exhibit a degree of resistance since they are adapted to acidic conditions with the gastrointestinal tract.

Alcohols alone, even at concentrations of 70% (v/v) have been shown to have low virucidal efficiency, but in combination with other active ingredients may be more effective. The use of phenol as a specific virucide has also been questioned (Lloyd-Evans *et al*, 1986).

In addition to protein precipitants, lipid solvents such as ether can be used as biocides. However, these attack the lipids in the viral envelope, so are only applicable to enveloped viruses such as influenza, herpes, measles and mumps viruses. Those occurring in sewage are generally not enveloped viruses, therefore are not susceptible to lipid solvents.

10.7 Filtration

Other methods which have been considered for the removal of microorganisms from water include filtration, microfiltration and reverse osmosis.

Filtration through cellulose acetate membrane filters of 0.22 um pore size is routinely used for removing bacteria from suspension. Positively charged filters have been used to concentrate viruses from tap water, while membrane filters can adsorb viruses when the pH is reduced to below their isoeletric point. Although filtration methods are suitable for clean water, problems of solids interference preclude their use for wastewaters. The high solids concentrations and the small pore sizes necessary to ensure removal of individual virions mean that filtration methods would be largely impractical for crude sewage. Studies on cross-flow microfiltration (pore size approximately 90 um) of mixed liquor at the University of Newcastle have found that clogging occurs after 10 days. As a tertiary treatment for secondary effluent however, it may be more successful; pilot studies are currently being carried out on anaerobic effluents.

Ultrafiltration has been investigated for wastewater disinfection in France (Fressonnet-Chambarlhac *et al*, 1983a). The system was found to be sensitive to operational problems and breakdowns. Although giving good removal of total and faecal coliforms and faecal streptococci, the problem remained of disposal of the concentrate containing the microorganisms. It was concluded that the process would only be viable for small, well supervised plants.

10.8 Ultrasound

Ultrasonication can be used to inactivate microorganisms; cells are broken up by ultrasonication or vibration at up to 700,000 cycles s^{-1} in liquid suspension (Hawker and Linton, 1979. Inactivation is caused by the physical destruction of the cell.

However, it is more frequently applied as a recovery method for separating both bacteria and viruses from solids. Ultrasonication effectively increases the numbers of microorganisms by disaggregating flocs and releasing encapsulated cells. It has been proposed as a pretreatment method for UV disinfection of wastewaters. A 20kHz, 300 W probe applied for 5 min was shown to increase bacterial counts by 2-5 fold; subsequent UV irradiation showed a much higher bacterial kill than in samples which did not receive ultrasonication pretreatment (Oliver and Cosgrove, 1975). Ultrasonic treatment before and during ozonation has also been shown to increase the sensitivity of viruses to disinfection (Harakeh and Butler, 1985). A preparation of poliovirus ultrasonicated for 2 min at 20MHzs^{-1} (100W) and exposed to 0.1mgl^{-1} of ozone increased the kill from <90% to 99.5% (Katzenelson *et al*, 1974).

It is possible that resonant frequencies would differ for different groups of microorganisms; considerable development of the methodology would be required for its application to wastewaters as a complete disinfection treatment. However, it would appear to offer a useful pretreatment technique for ozone or UV disinfection and, depending a cost considerations, may merit further investigation.

11 COMPARISON OF DISINFECTION ALTERNATIVES

11.1 Comparison of inactivation efficiencies

Comparison of the efficiencies of alternative disinfectants is difficult because of the wide range of procedures, experimental conditions and microorganisms employed in the various studies reported. Studies which give a direct comparison of the different disinfectants are useful but tend to be specific to a particular set of experimental conditions. However, from a review of the literature, a number of general conclusions can be drawn. One of the most important is that the quality of the effluent is particularly influential and may account for the wide discrepancy in the values for disinfection efficiency quoted.

The use of mathematical concepts based on inactivation kinetics to predict disinfectant concentrations and contact times needed, enables comparisons to be made of a range of disinfectants under similar conditions. Under controlled conditions, microorganism inactivation rates can be considered to have the characteristics of a first order chemical reaction and several studies have employed the use of a model, as follows:

$$K=C^nt$$

Where C = disinfectant concentration (mgl^{-1})
t = time (min)
K = constant

The constant, K, is specific for a particular microorganism and set of conditions. The value of n has been found to be equal to 1 for a range of microorganisms but extrapolation of Ct is generally valid for at least 2-3 orders of magnitude of inactivation for most microorganisms (Hoff, 1986). A summary of Ct values for 99% inactivation of various microorganisms is shown in Tables 11.1 and 11.2.

Table 11.1: A summary of Ct (concentration x time, mgl^{-1} min) values for 99% inactivation of various microorganisms at 5°C in demand free situation (Hoff, 1986)

Microorganism	HOCl pH 6-7	NH_2Cl pH 8-9	ClO_2 pH 6-7	O_3 pH 6-7	UV*
E.coli	0.034-.05	95-180	0.4-.75	0.02	0.007
Poliovirus I	1.1-2.5	768-3740	0.2-6.7	0.1-0.2	0.022
Rotavirus	0.01-.05	3806-6476	0.2-2.1	0.006-.06	0.025
bacteriophage f_2	0.08-.18				
G. lamblia cyst	47->150			0.5-0.6	
G. muris	30-630		7.2-18.5	1.8-2.0	
A. castellanii cyst					0.105

* Ct values in Ws cm^{-2} (Chang,1986)

Table 11.2: A summary of Ct values for 99% inactivation of various microorganisms (Olivieri, 1985)

Microorganism	HOCl pH6,5°C	NH_2Cl pH9,15°C	ClO_2 pH7,25°C	O_3 pH7
E.coli	0.04	64	0.28	0.002[b]
Poliovirus I	2.0	900	1.9	0.42[c]
Entamoeba histolytica cysts	20[a]			1.5[d]

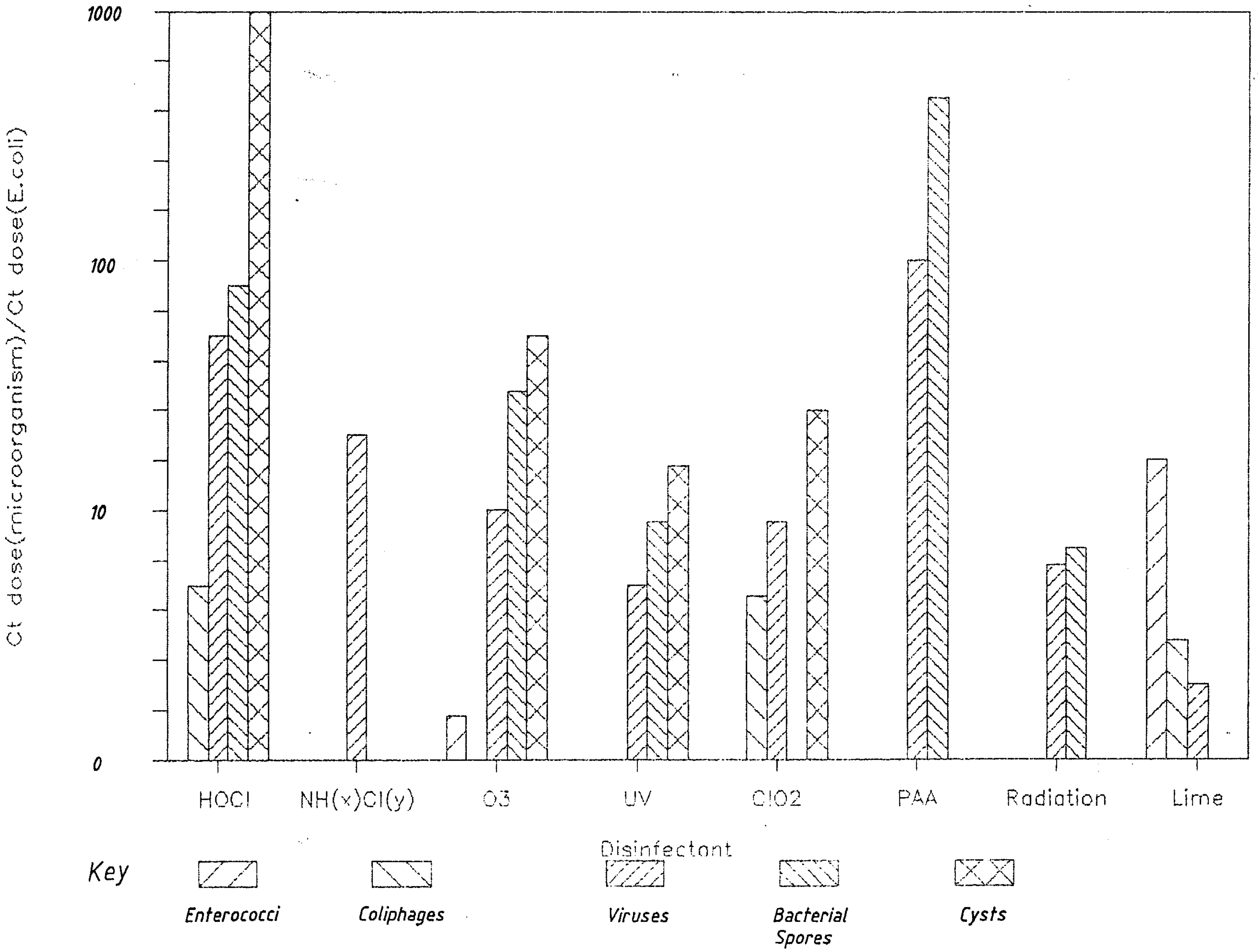
*[a] pH 7, 30°C
[b] pH 7, 12°C
[c] pH 7, 25°C
[d] pH 7.5-8.0, 19°C

Data from Olivieri (1985) show lower Ct values at the higher temperatures but are generally consistent with those of Hoff (1986). The results clearly indicate the increased resistance of viruses and protozoan cysts compared to *E.coli*, regardless of the nature of the disinfectant. Given sufficient concentration and contact time, the disinfectants could destroy all bacteria and viruses, but a marked difference in Ct values means it is possible that most or all of the indicator bacteria could be destroyed while many viruses still survive. Thus the use of indicator organisms would only be valid when the range of Ct values for a particular disinfectant is relatively narrow.

A graphical representation of approximate Ct values for a range of microorganisms relative to *E.coli* for the different disinfectants is shown in Figure 11.1. Whilst in the case of chlorine and ozone this represents the work of several studies on specific Ct values, in others approximate values have been estimated from operational data or reported efficiencies. It should therefore only be regarded as semi-quantitative. However it gives an indication of the relatively narrow inactivation range of chlorine dioxide, UV and ozone for the inactivation of highly resistant pathogens (cysts) compared to *E.coli*. Ozone, UV and radiation can also be seen to have a narrow inactivation range for viruses. Free chlorine (HOCl) appears to be relatively ineffective, particularly against cysts, and demonstrates that combined chlorine residuals are as effective against poliovirus relative to *E.coli* as HOCl. PAA also exhibits a wide inactivation range for the more resistant microorganisms in comparison to coliforms. Viruses have been reported as more susceptible than bacteria to lime at high pH (Grabow, 1978) but this has yet to be verified by other studies.

Whilst most comparative disinfection studies have considered chemical disinfectants only, Chang *et al* (1985) evaluated the UV dose required to inactivate pathogens and indicator organisms in secondary effluent. The dosages of UV light required for a 3 log reduction of cultured bacteria, total coliforms and standard plate

Figure 11.1: Inactivation ranges for different micro-organisms relative to E.coli for alternative disinfectants



count organisms were of a similar magnitude, but those for viruses, bacterial spores and aemobic cysts were 3-4 times, 9 times and 15 times higher than the dose for *E.coli* respectively. Equating the Ct dose ($mgminl^{-1}$) with a UV dose ($Wscm^{-2}$), it is evident that UV has a much narrower inactivation range than chlorine (Table 11.1).

The relationship $K=C^nt$ for 99% reduction of microorganisms was also found to be valid in studies on the relative efficiencies of chlorine, ozone and UV on both enteric and spore-forming bacteria and an infectious yeast (Kawamura *et al*, 1986). The reduction profiles for the various microorganisms showed that the contact time could be reduced effectively with the use of ozone; a residual of 1 mgl^{-1} achieved 99% inactivation within a few minutes, a factor of 100 smaller than that for chlorine. UV iradiation was unique in that the disinfecting power continued at low microbial concentrations and also inactivated spore-forming bacteria and *Candida tropicalis* more effectively than chlorine, though they were equally effective bactericides.

Though these studies are useful in providing comparative values under carefully controlled conditions, in practice, a number of factors will alter the first order relationship, including microbial aggregation and association with particulate materials. Disinfectant concentrations and contact times will be much greater in practice and depend on the wastewater quality, in particular the presence of particulate matter. Studies conducted on wastewater effluent therefore provide a more representative picture of inactivation efficiencies likely to be achieved in the field. The smaller size of viruses means that they can be protected from disinfectant contact by much smaller particles than those which protect bacteria and cysts, and they are therefore likely to show higher resistivity under field conditions in comparison to bacteria.

A comparative study of chlorine chlorine dioxide, ozone and PAA against representative enteric viruses and a bacteriophage in activated sludge effluent was carried out by Harakeh (1987). There was a characteristic biphasic mode of inactivation with a sharp decrease in viral numbers within the first 5 min followed by an extended phase with little further inactivation after 30 min. There was considerable variation in the response of the viruses as well as a difference in the efficacy of the disinfectants tested, which was cited as an indication of the inappropriateness of a model virus. Ozone was found to be the most efficient disinfectant with residual concentrations as low as 0.5 mgl^{-1} required for complete inactivation in 5 min, compared to residuals of 5 mgl^{-1} for chlorine dioxide, 11 mgl^{-1} for chlorine and a concentration of 140 mgl^{-1} of PAA for equivalent disinfection.

Pilot studies conducted by Rivoal (1983) on wastewater effluent also confirmed the efficiencies of ozone and chlorine dioxide as disinfectants compared to chlorine (Table 11.3). A similar log abatement of bacteria was achieved by an ozone residual of 0.5 mgl^{-1} and a chlorine dioxide residual of 1.5-2 mgl^{-1} at 15 min contact time whilst chlorine residuals of 2.5 mgl^{-1} at 30 min contact time were necessary. UV inactivation was characterised by the short contact time required, which is of the order of seconds rather than minutes. The difficulties of comparing a physical and chemical dose was overcome by equating a UV dose of $mWs\ cm^{-2}$ with a chemical dose of $mg\ minl^{-1}$.

Similarly, experiments conducted on secondary wastewater at Montpellier, France (Fressonnett-Chambarlhac *et al*, 1983a) permitted a comparison between the bactericidal and virucidal efficiencies of chlorine, chlorine/bromine, bromine, chlorine dioxide and ozone. The bactericidal and virucidal properties of the disinfectants were assessed on biologically treated domestic effluent that had been clarified, filtered or microstrained. Whilst the effluent subjected to additional treatments was improved in terms of COD and suspended solids, there was little alteration in the bacteriological quality or concentrations of

Table 11.3: Comparative disinfectant doses and contact times to achieve a 3-4 log reduction in coliforms (Rivoal, 1983)

Disinfectant	Wastewater	Dose (mgl^{-1})	Residual conc. (mgl^{-1})	contact time (mins)	inactivation efficiency for total coliforms (log)
chlorine	primary	12	-	30	4-5
	secondary	-	2.5	30	4
ozone	secondary	-	0.5	15-20	4
chlorine -bromine	secondary	5-10	-	20	4
chlorine dioxide	secondary	-	1.5-2	15	4
UV	-	100*		0.15	3**

* UV dose in $mWscm^{-2}$

** faecal coliforms

ammonia-nitrogen. Table 11.4 shows the dosages and contact times required for a 3 log reduction of bacteria in the clarified effluent. The results, given in table 11.5, generally confirm those obtained from other studies conducted under demand free conditions, in terms of the range of doses required to inactivate the different types of microorganisms.

Chlorine required a minimum contact time of 30 min, due to the slower disinfectant properties of the combined chloramines. For a 3 log reduction in total coliforms, faecal coliforms and faecal streptococci, a 3.5-4.1 mgl^{-1} dose and 2-2.6 mgl^{-1} residual in clarified effluent was required; and a 2.5-3.4 mgl^{-1} dose, 1.1-2.1 mgl^{-1} residual in filtered effluent. However chlorine appeared less efficient as a virucide. In addition, a residual level of approximately 0.02 mgl^{-1} chlorine is potentially toxic to aquatic organisms and necessitates dechlorination prior to discharge. The formation of haloforms was observed during the study but the concentrations observed were never greater than 7 ulm^{-3}.

The use of prechlorination followed by bromine addition led to high chlorine residuals due to the weak chlorine demand of the effluent, whereas the use of bromine alone allowed a shorter contact time. The dose varied widely with effluent quality; 4.1 mgl^{-1} bromine in clarified effluent and 0.8 mgl^{-1} bromine in filtered effluent was required for a 3 log reduction in faecal coliforms. With the chlorine/bromine treatment, 13 ulm^{-3} dibromochloromethane ($CHClBr_2$) and 5 ulm^{-3} dibromomethane (CH_2Br_2) were observed, whilst with bromine alone the by-products were formed at lower concentrations. The resultant bromamines are considered to be less likely to prove toxic due to their instability.

Chlorine dioxide was found to be the most effective disinfectant tested, characterised by its rapidity and low dosage. A 1.1-4.5 mgl^{-1} dosage and a residual of less than 0.5 mgl^{-1} chlorine

Table 11.4: Disinfectant dose and contact time necessary to achieve a 3 log abatement of faecal coliforms in clarified secondary effluent (Fressonnet - Chambarlhac *et al*, 1983a)

Disinfectant	Dose (mgl^{-1})	Residual concentration (mgl^{-1})	Contact time (min)
Chlorine	3.5-4.1	2-2.6	40
Chlorine-bromine	3.8-4.6	1.5	40
Bromine	4.1	-	40
Chlorine dioxide	4.5	0.7	10
Ozone: (air)	4.8-7.7	0.1-0.5	)13-15
(oxygen)	7.5-11	0.13-1.3	)

Table 11.5: Relative disinfectant dose rates to reduce microbial levels (Fressonnet-Chambarlhac *et al*, 1983a)

	Dose necessary to obtain identical abatements (mgl^{-1})		
Disinfectant	Faecal Coliforms	Enteroviruses	Coliphages
Chlorine	1	4-20	4.5-10
Chlorine-bromine	1	2-3	1.5-2.6
Chlorine dioxide	1	1.5-4	0.6-1.2
Ozone	1	3-15	1.5-10
UV	1*	3-4*	

* Chang (1985)

dioxide achieved a 3 log abatement of coliforms and faecal streptococci in 10 min. In addition, it proved an effective virucide. The by-products, in particular chlorite (ClO_2^-) have a well characterised toxicity, however, the hazards associated with its production and handling are the major drawback in its application.

The efficiency of ozone as a disinfectant was found to be strongly dependent on the effluent quality. Ozone has a tendency to react with organics and reductants at the expense of disinfection. The difference in the two modes of production of ozone, due to the ratio of gas to effluent, was more evident in treatment of the clarified effluent than the filtered effluent. A 4-8 mgl^{-1} dose and 0.1-0.5 mgl^{-1} residual of ozone from air was required for a 3 log reduction in coliforms and faecal streptococci at 15 min contact time, whereas oxygen-produced ozone required a 5-11 mgl^{-1} dose and 0.13-1.3 mgl^{-1} residual for comparable inactivation. After chlorine dioxide, ozone was found to be the most efficient treatment. The study did not find evidence of organic by-product formation or toxicity (the ozone residuals are short-lived), on the contrary, the saturation of the effluent with dissolved oxygen was thought to be favourable. The improvement in effluent quality and absence of permanent toxicity makes ozone an attractive proposition and only the great variability of ozone demand with effluent quality was a disadvantage.

Though no results were presented, it was reported that UV proved effective. In addition, the lack of toxic residual made it a satisfactory method in terms of its environmental impact. The relative safety and simplicity of the process was considered to recommend it for use at small installations for effluents of a high quality (Fressonet-Chambarlhac *et al*, 1988).

In summarising the results of the above studies, it appears that the most effective disinfectants in terms of the range of doses required for viral and bacterial inactivation are chlorine dioxide followed by ozone. UV also appears effective though the difficulties in measuring the dose and the use of different units does not facilitate direct comparison. The halogens, bromine chloride and bromine, are more effective than chlorine as virucides, though as bactericides their efficacies are more comparable. PAA requires prohibitively large doses to be effective as a virucide. Chlorine, both free and combined, is an efficient bactericide but its use as a virucide appears limited.

11.2 Comparison of costs

11.2.1 Reported cost comparisons

The reported costs for the different disinfectants vary widely depending critically on the wastewater quality, effluent standards, currency rates and year of calculation, together with whether or not costs are inclusive of civil engineering works. Whilst comparisons between reported costs of different disinfectants are of limited use, several studies have made direct comparisons between disinfectants based on specific wastewater qualities and effluent targets. These are useful in gauging relative differences in costs between the processes.

One such comparison compiled by Whitby *et al* (1984) was taken from the 'Innovative and Alternative Technology Assessment Manual' with costs updated to 1982, a 15 year amortisation period and a 12% interest rate. The figures, shown in Table 11.6, take capital and operating costs for 4 installation sizes compared to a base figure of 1 for the UV process. From this analysis it is apparent that UV is the most cost effective process both in terms of capital and operating costs with the exception of the larger chlorination plant. Ozone is some 7 to 9 times more costly than UV and 2-3 times more costly than chlorination. The dechlorination process appears to add 20-30% to the cost of the chlorination process.

A more detailed cost analysis was compiled by Rivoal (1983) for a

Table 11.6: Comparison of relative capital and operating costs for alternative disinfection processes (Whitby *et al*, 1984)

Process	Plant size ($10^3 m^3 d^{-1}$)			
	3.78	18.9	37.8	378
Capital				
chlorination	2.01	1.76	1.45	0.86
chlor/dechlorination	2.69	2.24	1.81	1.00
ozonation by air	9.98	7.46	7.28	6.96
UV	1	1	1	1
Operating				
Chlorination	2.77	2.46	2.11	1.47
chlor/dechlorination	3.96	3.36	2.84	1.88
ozonation by air	8.67	6.87	6.73	7.05
UV	1	1	1	1

range of disinfectant processes. Based on a matrix of 3 effluent qualities and for continuous and batch flow processes, costs were estimated for 4 sizes of installation. The disinfection processes considered were chlorine (as chlorine or sodium hypochlorite, both with and without dechlorination), ozone (from air), chlorine dioxide, chlorine/bromine (to prevent excessive bromine consumption) and UV. Two types of installation were considered in the cost analysis. The first was a continuous treatment process with closed-loop control of the incoming effluent and dosage, and the second a batch-flow process.

The installations were sized to treat effluent from populations of 1000, 5000, 25000 and 75000 people. Assuming 0.15 m^3d^{-1} per person, this is equivalent to plant sizes ranging from 150 m^3d^{-1} to $11250m^3d^{-1}$. The disinfectant doses and estimates are shown in Table 11.7. Costs are reported here only for secondary effluent; although costs were generally higher for primary effluent the relative differences in cost between disinfection alternatives were similar.

A comparison of both capital and operation and maintenance costs relative to chlorination for continuous flow treatment of a secondary effluent is shown in Table 11.8. Investment costs include civil engineering requirements, contact basins plus aerators, pumps, ozonators and UV lamps.

For the small size plant of $150m^3d^{-1}$ the investment costs ranged from £9000-65,000. (These costs represent the current sterling equivalent of the 1981 value in French Francs). Gaseous chlorine, hypochlorite and UV were the cheapest processes and ozone the most expensive. In spite of the high energy costs for aerators and pumps, the batch flow processes were more economical for all plant sizes in the case of ozone and UV and for the small and medium plants in the case of the halogens. Dechlorination added 20% to the cost of the investment so that it approached the cost of chlorine/bromine, chlorine dioxide and UV for the small

Table 11.7: Disinfectant doses and contact times used as a basis for cost analysis (Rivoal, 1983)

	Cl_2	O_3	ClO_2	Cl/Br	UV
contact time (min)	30	20	15	20	0.3
dose (mgl^{-1})*					
Primary effluent	10.5	17	5.5	7.6	750
physico-chemical effluent	9.2	15	5.5	7.2	750
secondary effluent	5.5	8.5	3	4.3	550
secondary-nitrified effluent	4	8	3	3.3	550

*UV dose in mWs cm^{-2}

Table 11.8: Comparison of capital and operating costs relative to gaseous chlorine for a range of disinfection processes and plant sizes in a continuous flow treatment of secondary effluent (Rivoal, 1983).

Plant size (m^3d^{-1})	Cl_2	Cl_2 /SO_2	NaOCl	NaOCl /SO_2	O_3	Cl_2 /Br_2	ClO_2	UV
Capital								
150	1	1.9	0.8	1.7	2.1	1.6	2.1	0.9
750	1	1.8	0.7	1.5	3.0	1.4	1.8	1.3
3750	1	1.6	0.7	1.3	6.8	1.3	1.4	3.2
11250	1	1.3	0.6	1.0	9.8	1.2	1.0	5.1
Operating								
150	1	1.7	1.1	1.8	1.4	1.6	1.9	1.0
750	1	1.6	1.1	1.7	2.1	1.5	1.7	1.2
3750	1	1.6	1.2	1.8	4.0	1.6	1.7	2.2
11250	1	1.6	1.5	2.0	6.8	1.8	2.2	3.9

facilities. For the larger facilities the costs of the halogens became more comparable whilst that of ozone and UV rose disproportionately. For the 11,250 m^3d^{-1} plant, investment costs ranged from around £50,000-1,300,000, with ozone 3-10 times and UV 2-5 times more expensive than chlorine respectively. However this difference was less marked for the batch process.

Operation and maintenance costs were reported to rise accordingly with the size of the installation and showed distinct economy of scale. For the 150 m^3d^{-1} plant, costs ranged from approximately £3000-6000 p.a. whilst for the 11250 m^3d^{-1} facility the costs were £13,000-88,000 p.a. Chlorine and hypochlorite were found to have the lowest running costs followed by UV at the smaller facilities. When dechlorination processes were taken into account the halogens showed costs of a comparable magnitude. Operating costs for ozone started to become significant at the larger installations but were actually lower than the chlorination/dechlorination process at the smallest plant. The batch flow process was more economical for ozone and UV for all plant sizes and also for chlorine dioxide and bromine chloride at the smaller facilities.

Tables 11.9 and 11.10 show the annual total costs for both continuous and batch flow disinfection of primary and secondary effluent. Comparison of total costs for the continuous and batch flow processes showed that investment in the former is economically justified for all installations and for all disinfection processes operating on secondary effluent. Up to a plant size of 750 m^3d^{-1}, chlorine was the most economic process though addition of a dechlorination system made it economically comparable with other halogens. At 3750 m^3d^{-1} the costs of ozone started to become substantially higher than the other processes. All disinfection processes showed distinct economies of scale and disinfection at the smallest size facility was markedly more costly, particularly for the batch flow process.

Table 11.9: Annual total costs (pm^{-3})* for continuous and batch flow treatment of primary effluent (Rivoal, 1983)

Plant Size (m^3d^{-1})	Treatment	$Cl_2(g)$	Cl_2/SO_2	NaOCl	NaOCl/ SO2	O_3	Cl_2-Br_2	ClO_2	UV
150$^+$	Continuous	8.0	10.7	8.0	11.1	18.4	10.9	13.9	8.9
	Batch flow	13.1	24.0	12.1	23.0	28.0	21.1	26.4	14.1
750	Continuous	3.4	4.4	3.3	4.3	7.5	4.1	4.8	3.9
	Batch flow	3.7	6.3	3.3	5.9	10.3	5.3	6.4	6.8
3750	Continuous	1.9	2.3	1.8	2.3	4.7	2.1	2.4	2.3
	Batch flow	1.5	2.3	1.4	2.2	8.9	1.9	2.3	5.4
11250	Continuous	1.2	1.5	1.4	1.6	4.2	1.6	1.9	2.2
	Batch flow	0.8	1.2	0.9	1.2	7.7	1.2	1.5	4.8

* Conversion of 1983 French Franc value at 1988 exchange rate of 1FF = £0.99

\+ for physico chemical treatment

Table 11.10: Annual total costs (pm^{-3})* for continuous and batch flow disinfection of secondary effluent (Rivoal, 1983)

Plant Size (m^3d^{-1})	Treatment	Cl_2(g)	Cl_2 /SO_2	NaOCl	NaOCl /SO2	O_3	Cl_2 -Br_2	ClO_2	UV
150	Continuous	6.2	8.9	6.3	9.3	15.0	9.4	11.7	7.0
	Batch flow	12.8	23.4	11.7	22.6	21.7	20.8	26.0	12.9
750	Continuous	2.4	3.1	2.2	3.0	5.6	3.0	3.6	2.7
	Batch flow	3.4	5.7	3.0	5.3	8.3	5.0	5.9	4.9
3,750	Continuous	1.0	1.4	1.1	1.4	2.8	1.3	1.5	1.7
	Batch flow	1.1	1.7	1.1	1.7	5.7	1.6	1.7	3.9
11,250	Continuous	0.7	0.9	0.7	0.9	2.4	1.0	0.9	1.5
	Batch flow	0.6	0.9	0.6	0.9	5.2	0.9	1.0	3.7

* conversion of 1981 French Franc value at 1988 exchange rate of 1FF = £0.99

From the above studies, it can be seen that the relative costs of the different processes are specific to a particular plant size. For example, chlorine shows distinct economies of scale and whilst there is no technical limit on the size of an UV plant the costs tend to become prohibitive because of the high operating costs, at the larger facilities. On an economic basis, chlorine, hypochlorite and UV (at the small-medium plants) are the most cost effective. However this does not take into account any remedial costs for precluding adverse environmental effects, eg. by dechlorination. A dechlorination system, necessary to prevent residual chlorine toxicity, adds 20-30% to the costs of chlorine and sodium hypochlorite systems, and makes them comparable with the costs of the halogens such as bromine chloride and chlorine dioxide. Also the additional benefits of a process such as colour removal with ozone or phenol destruction with chlorine dioxide, are not accounted for in a simple cost analysis. Though the data from Rivoal (1983) show slightly smaller differentials between the processes, possibly because of the smaller range of plant sizes, ozone is still some 2-8 times more costly than chlorine. Sodium hypochlorite is approximately equal to chlorine on an economic basis, whilst chlorine dioxide and bromine/chlorine are up to two times as expensive as chlorine.

11.2.2 Case study costs

Obtaining direct comparisons between processes from the literature allows relative costs to be evaluated but these will still be specific to a particular effluent quality and standard. Furthermore, differential power, capital and labour costs for foreign plants limit the validity of direct cost conversions. To obtain figures applicable to the UK and the disinfection of sewage prior to marine discharge, a theoretical case study was devised and manufacturers asked to draw up budget costs. Details of the basis for the case study and the respective manufacturers are shown in Table 11.11.

Table 11.11: Disinfectants considered in the case study and respective manufacturers

Process	Manufacturer
chlorine (gaseous)	Portacel
sodium hypochlorite	ICI
OSEC	Wallace and Tiernan
UV	Hanovia
ozone	Ozotech
Clarifloc*	Blue Circle
PAA*	Interox

* cost data obtained from published material

An outfall situated in a typical coastal area, serves a population of 25,000 which @ 180 ld^{-1} flow gives a DWF of 4,500 m^3d^{-1}.

For a separate sewerage system, maximum flow = 3DWF
For a combined sewerage system, maximum flow = 6DWF

Assuming a design dose at 4.5DWF, which represents a reasonable combination of combined and separate systems, this would give 75% of design dose at 6DWF and the ability (if desired on occasion) to achieve 150% of design dose at 3DWF. Retention times have been based on 4.5DWF. Therefore, the design flow rate used for the comparison was 4,500 x 4.5 = 20,250, say 21,000 m^3d^{-1}. The Clariflow costs were based on those for Sandown, which was sized for a 3DWF summer flow of 21,000 m^3d^{-1}.

Cost estimates have been developed for application of the various disinfection processes in the UK at 1988 prices. Capital cost estimates (including design and supervision costs) have been amortised at a rate of 9% per annum over periods of 15 and 40

Table 11.12: Summary of estimated total treatment costs (1988) for hypothetical UK application of disinfection processes

Disinfection process	Total cost (pm^{-3})[1]			
	Screened raw sewage		Biologically treated sewage	
	6 month operation	12 month operation	6 month operation	12 month operation
gaseous chlorine[2]	2.0-5.5[3]	1.6-5.1	(1.4)[4]	(1.1)
hypochlorite solution[2]	2.1-7.0	1.7-6.6	(1.5)	(1.2)
on-site electrolytic chlorination	3.8-15.2	2.4-9.6	(2.6)	(1.6)
ozone	no data assume=20	no data assume=13	12.8	7.3
ultraviolet irradiation	not appropriate	not appropriate	4.9	3.5
peracetic acid	11.6	10.9	(4.0)	(3.5)
Clariflow[5]	26.9	18.5	not appropriate	not appropriate

[1] based on 1988 prices - includes amortised capital costs (as discussed in text) and full operation and maintenance

[2] if dechlorination using sulphur dioxide was adopted, costs could increase by approximately one third

[3] range of costs based on a low (20 mgl^{-1}) and high (100 mgl^{-1}) dosages.

[4] figures in parentheses are approximate estimates for low dosages extrapolated from raw sewage applications

[5] costs influenced significantly by local sludge disposal situation

years for equipment and civil engineering items respectively.

Power costs were calculated on the basis of 5.5 $pkWh^{-1}$ although in some local instances power costs of 4 $pkWh^{-1}$ or less may be available. For nearly all processes, power costs do not represent a major element of the total cost. Average labour costs have been assumed to be £12 h^{-1} to include payroll and overhead elements. The costs have not allowed for land costs, which may be significant in the case of the Clariflow process.

The costs are given in full in Appendix I and are summarised in Table 11.12. From this it can be seen that the costs of disinfecting crude sewage, for which not all systems are appropriate, increase according to the following series;

Cl_2(gas) < Cl_2(hypo) < Cl_2(OSEC), PAA < Clariflow

The costs of chlorination would increase by approximately one third if dechlorination were required. Capital investment for sulphur dioxide would be comparable to that for gaseous chlorine since the dosing systems are similar. Operational costs would be dependent on the chlorine residual generated, since this determines sulphur dioxide dosing on a 1:1 basis. Chemical costs for sulphur dioxide are comparable to those of chlorine.

As with all chemical disinfectant systems, there is greatest sensitivity of cost to dose. The costs given for chlorine are based on a dosage of 20 mgl^{-1}, typically used in pilot studies, whilst estimates have also been made for a hypochlorite dose of 100-120 mgl^{-1} available chlorine, reflecting UK experience at Weston-Super-Mare. Even at the higher dose, chlorine remains the cheapest option, although the cost of OSEC becomes comparable to that of PAA.

The Clariflow process is the most expensive option, with a total cost approaching that of land-based treatment. However, the system does have additional benefits such as removal of BOD, SS and heavy metals. There are insuffient data to evaluate the costs of ozonation of crude sewage because it is generally only used for treated effluents. Assumed costs based on the latter are intermediate between PAA and Clariflow.

For the disinfection of secondary effluents, costs increase as follows;

Cl_2(gas) < Cl_2(hypo) < Cl_2(OSEC) < UV, PAA < O_3

There is a smaller range between alternatives for treated effluents; UV appears attractive particularly if compared with chlorination plus dechlorination, and is of a similar cost to PAA. Ozone remains one of the most expensive options. The comparative magnitude of costs given in Table 11.12 is similar to that reported for operational plants; absolute costs vary with plant size and effluent quality.

11.3 Comparison of residual toxicity and by-product formation

11.3.1 Residual toxicity

Quantification of residual toxicity, resulting from toxicity of parent compounds to receiving marine biota, may be be approached by consideration of the acute toxicity (LC_{50}) tests that have been conducted on a number of freshwater and marine organisms. While these tests are for the parent compound only and do not address the question of toxicity of by-products, the values indicate the potential effects of a worst possible case such as a chemical spill or overdose. Consideration of the LC_{50} concentrations should also take into account the half-life of a compound. While in potable water disinfection the presence of a long-lived residual is necessary to safeguard health, it is undesirable in marine discharge where the chemical residual may cause adverse effects in the receiving environment. A long-lived residual such as chlorine (combined) will be potentially more of a problem than a short lived residual such as ozone which dissipates rapidly from water. Thus in ozone toxicity testing, the high residual concentrations used to induce effects would be unlikely to occur in practice. An extensive toxicity database has been compiled by Hubly *et al* (1985) for chlorine and ozone. Table 11.13 summarises some results of toxicity tests.

Studies by Ward and De Graeve (1980) on the toxicity of chlorine, bromine chloride and ozone in effluent with a large non-domestic component found that residual chlorine exhibited the greatest toxicity, although this could be effectively eliminated by dechlorination with sulphur dioxide. Residual ozone produced mortality under special conditions where the test animals were exposed to the effluent immediately after it was contacted with ozone. However, the fact that the effluent was filtered prior to ozonation may have contributed to the reduced toxicity. In these tests ozone was sufficiently toxic to cause mortality in concentration ranges of 0.088-0.288 mgl^{-1}. In the routine tests, the highest ozone residual measured was only 0.012 mgl^{-1}, with the majority in the range 0,.002-0.008 mgl^{-1}.

Chlorine bromide produced similar mortality in fish to chlorine, with the exception of salmonids which were more sensitive. This was in direct contrast to earlier studies conducted with domestic effluent at Grandville (Ward *et al*, 1976); the different response was thought to be due to some synergistic or additive action with an industrial component of the effluent. Liden *et al* (1980) also confirmed that the toxic effects of bromine chloride and chlorine were similar for condenser cooling effluents on selected estuarine species.

Lethal concentration and effect concentration values have been established for PAA in work by Interox. The lethal concentration doses appear significantly higher than for alternative disinfectants, however the values are not directly comparable. It should be noted that values quoted for Cl_2, O_3, BrCl etc are for residual levels whereas the values for PAA refer to the original dosage. Whilst PAA is short lived and is unlikely to be

Table 11.13: Summary of toxicity tests conducted on a variety of disinfectants

Disinfectant	Test Species	Test	Residual concentration ($mg l^{-1}$)	Reference
Chlorine	Rainbow trout	96 LC_{50}	0.023	White(1986)
	Fathead minnows	96 LC_{50}	<0.1	White(1986)
	Pugnose shiner	96 LC_{50}	0.029	Ward(1980)
	Goldfish	96 LC_{50}	0.519	Ward(1980)
	Fish	94 LC_{50}	0.08-0.26	Arthur et al Mount(1975)
	Blue crabs	96 LC_{50}	0.84-0.86	Laird and Roberts
	Invertebrates	94 LC_{50}	0.21->0.81	Arthur et al (1980)
Bromine chloride	Pugnose shiner	96 LC_{50}	0.01	Ward (1980)
	Rainbow trout	96 LC_{50}	0.017	
Ozone	Lake trout	96 LC_{50}	0.088	Ward (1980)
	goldfish	96 LC_{50}	0.288*	
	Fathead minnows	94 LC_{50}	0.2-0.3*	Arthur et al (1975)
	White perch		No mortality	Meldrim (1981)
	(i) estuarine	ILC_{50}(96,2)	at 0.68	
	(ii) freshwater	ILC_{50}(96,2)	at 0.28	
PAA[a] (Oxymaster)	Plaice	96 LC_{50}	10.7	Interox
	Brown shrimp	96 LC_{50}	15.2	
	Common mussel	48 EC50[+]	0.26	
	Pacific oyster	48 EC_{50}	0.27	
Hydrogen[a] peroxide	Fingerling Rainbow Trout	toxicity increased linearly with concentration	>40	Eden (1951) et al
	Roach	complete kill		
		1-5 h	100	
		5 h	50	

* It is unlikely that fish would encounter such high O_3 levels

\+ Development to D stage.

a Concentration as dose rather than residual seen at concentrations as high as 10 mgl^{-1} even at the site of outfalls, the relatively low effect concentrations on shellfish are an indication of the potential consequences of long term usage or over-dosing. However, the effects of PAA cannot be considered in isolation from those of hydrogen peroxide, which has a well-documented toxicity and mutagenicity.

An interesting observation made by Ward and De Graeve (1980) was that acute toxicity tests with non-disinfected effluent resulted in mortality in 8 out of 9 fish and 1 out of 7 invertebrate species tested, with mortality levels comparable to those of ozone and dechlorinated effluent. This suggested that the effluent rather than the disinfectant represented the toxic component. The ability of non-disinfected sewage to cause toxic and mutagenic effects has also been observed in studies by the Plymouth Marine Laboratory (PML, pers.comm.). Preliminary work suggests that the inherent toxicity/mutagenicity of sewage is dependent on its oxidation state, being lower under anaerobic conditions.

It is thought that the addition of disnfectants such as PAA may in some cases reduce the inherent genotoxicity of sewage by interfering with the causative microorganisms. Although a potentially beneficial effect, this does not mitigate the potential toxic effect of the disinfectant *per se*.

By their nature, all of the disinfectants are inherently toxic. However, their potential for residual toxicity effects on the marine environment is dependent on the half-life of the residual. Thus chlorine has the greatest potential for harm which laboratory studies and observed fish kill incidents arising from residual chlorine have demonstrated. The use of dechlorination with sulphur dioxide can attenuate toxicity. This is particularly important in relation to discharges to small rivers (as in many cases in the US), where the capacity for dilution is much less than for marine discharges.

Bromine residuals are generally shorter-lived and both bromine and bromine chloride have been shown to be less toxic than chlorine. However, if the effluent has a significant industrial component, there is the possibility that bromine chloride may react to form a by-product with a toxicity equal to that of chlorine. Whilst PAA may have a toxicity equal to that of chlorine, it is unlikely to have a significant effect in practice because it is unstable and short-lived.

Although demonstrably toxic, ozone appears to present few problems regarding residuals, due to its short-life and rapid dissipation from water. There is little available information on UV, which cannot exhibit a direct toxic effect but may cause a physical alteration of certain compounds and hence an indirect toxic effect.

11.3.2 By-product formation

The use of chemical disinfection of wastewater can result in the formation of more refractory and toxic compounds than those originally present. However, evaluation of the hazards associated with this requires indentification of a compound, often in the microgram concentration range, from the complex background of chemical 'noise' in seawater. This then has to be followed by laboratory and field tests to estimate the concentrations causing no adverse effects on marine organisms. The possibility of an additive or synergistic effect with other compounds and the lack of existing toxicological data further complicates the issue. Monitoring effects directly is sometimes possible as chronic or sublethal effects are often accompanied by an accumulation of the product in the body tissues of the affected organism, which may be hazardous to both the organism and its predators. However, effects on the abundance and diversity of a species, loss of habitat and avoidance are all more difficult to quantify and may not be immediately apparent.

Reports referring to the direct effects of potential disinfection by-products tend to be restricted to discussion of chlorine. Studies conducted by ICI (Pearson and McConnell, 1975) on the environmental concentrations and persistence of chlorinated hydrocarbons considered some simple C_1 and C_2 hydrocarbons. Table 11.14 shows the concentrations of chlorinated C_1 and C_2 hydrocarbons in Liverpool Bay seawater and their acute toxicity to selected marine organisms. The compounds chloroform, carbon tetrachloride, trichloroethane, trichloroethene and tetrachloroethene have all been identified in chlorinated secondary effluent (Glaze and Henderson, 1975; Bouwer, 1985). Hexachloro-butadiene was thought to arise as a by-product of the manufacture of commercial solvents. Table 11.14 shows that the concentrations of chlorinated hydrocarbons in seawater were at least three orders of magnitude lower than the corresponding LC_{50} values.

However, there is still a possibility of chronic or sublethal effects caused by lower concentrations. Furthermore, bioaccumulation may lead to tissue contaminant levels exceeding environmental concentrations. Laboratory experiments on bioaccumulation showed much higher concentrations of chlorinated compound in fatty tissues compared to muscle; when the organisms were returned to clean seawater, the concentrations of organochlorine in their tissues declined.

A review of the concentration of chlorinated hydrocarbons reported in marine organisms (Table 11.15) showed that the solvents trichloroethylene and perchlorethylene were widely distributed, as well as trichloroethane, chloroform and to a lesser extent carbon tetrachloride. The maximum overall increase in concentration between seawater and the tissues of animals at the top of the food chain ranged from 100-1000 fold, depending on the compound. The accumulation of chlorinated organics is manifested in many marine species; high residue levels of polychlorinated biphenyls (PCBs) have been found, especially in fish-eating animals in the higher

Table 11.14: Concentrations of chlorinated hydrocarbons found in Liverpool Bay sea water and their acute toxicity to marine organisms (Pearson and McConnell, 1975)

Compound	Average * concentration (ugl^{-1})	96h LC$_{50}$ to dab (mgl^{-1})	48h LC$_{50}$ to barnacle nauplii (mgl^{-1})	EC$_{50}$ unicellular algae (mgl^{-1})
trichloroethylene	0.3 (3.6)*	16	20	8
tetrachloroethylene	0.12 (2.6)	5	3.5	10.5
trichloroethane	0.25 (3.3)	33	7.5	5
chloroform	- (10)	28	-	-
carbon tetrachloride	0.25 (2.4)	ca.50	-	-
hexachlorobutadiene	0.004(0.03)	0.45	0.87	-

* Maximum concentration

Table 11.15 Concentration (ug kg^{-1} wet tissue) of chlorinated hydrocarbons in marine organisms (Pearson and McConnell, 1975)

Species		CCl_2CHCl	CCl_2CCl_2	CH_3Cl_3 +	CCl_4	$CHCl_3$
INVERTEBRATES						
plankton	0.05-0.4	0.05-0.5	0.03-10.7		0.04-0.9	0.02-0.9
Mytilus edulis	4-11.9	1.3-6.4		2.5-5.4		9-10
(oyster)						
Ostrea edulis	2	0.5		0.9	0.1	3
(oyster)						
Crangon crangon	16	3		2	6	45
(shrimp)						
FISH						
Pleuronectes platessa	flesh	0.8-8	4-8	0.7-7		NA
(plaice)	liver	16-20	11-28	2-47		NA
Platycthys flesus	flesh	3	2	4	2	21
(flounder)	liver	2	1	3	0.3	6
Limanda limanda	flesh	3 - 5	1.5-11	1.3-8		NA
(dab)	liver	12-21	15-30	2-14		NA
Gadus morrhua	flesh	0.8	<0.1	3.3		NA
(cod)	bladder	<0.1	3.6	NA		NA
BIRDS						
Sula bassana	liver	4.5-6	1.5-3.2	1.2-1.9		7.4
(gannet)	eggs	9-17	4.5-26	17-20		1.9-2.0
Alca torda	eggs	28-29	32-39	39.4-41		6.6-19.7
(razorbill)						
Uria aalge	eggs	23-26	19-29	35-43		8-65
(guillemot)						
MAMMALS						
Halichoerus grypus	bladder	2.5-7.2	0.6-19	16-30		7.6-22
(grey seal)	liver	3-6.2	0-3.2	0.3-4.6		0-12

trophic levels of marine communities (Reijinders, 1987). Deleterious effects resulting from organo-chlorine compounds have been reported in fish, seals in the Netherlands, Beluga whales in Canada and on Bluefish tuna (Zitko, 1987).

Whilst these chlorinated compounds are not all necessarily formed in wastewater chlorination, this demonstrates the ubiquity and efficiency with which chlorinated compounds become assimilated into the marine food web, and indicates the potential for their biomagnification. The pilot study by Welsh Water (see Section 2.9) dramatically illustrated the take-up of chlorine by-products in bivalves in seawater receiving chlorinated effluent. Nevertheless, concentrations declined five months after the end of the trial to levels comparable to those of pre-chlorination conditions. This has implications for seasonal disinfection, suggesting that there may be potential for a degree of purification of the biota during non-disinfection periods.

The effects of by-products formed by alternative disinfectants are still largely unquantified. Whilst the strongly oxidative nature of ozone, PAA and chlorine dioxide may be expected to alter the components of the effluent matrix, many of the oxidation products do not appear to be harmful. Although ozone oxidises a wide range of organic compounds, the products generally have no deleterious health effects with the exception of the possible formation of certain aldehydes and hydroperoxides. Increased mutagenic activity of ozonated recycled water has been observed and Jolley *et al* (1982) have identifed the possible production of mutagenic, non-volatile organic constituents.

In the same study, UV was found to cause only slight chemical changes in the chemical constituents. Although in one case UV produced some non-volatile mutagenic components, this was not observed in the separated fractions. The use of gamma-irradiation may be more likely to produce mutagenic effects, particularly at low dosages (Madeley, pers.comm.). Irradiation of wastewater is likely to produce free radicals which then give rise to stable radiolytic products and are subsequently converted into a large number of different products.

Chlorine dioxide is strongly oxidative, which enables it to react with a wide range of organic compounds. Unlike chlorine however, it generates no by-products such as THMs or chloramines, tending towards oxidation rather than halogenation reactions. Nevertheless, halogenated by-products may still arise if the chlorine-chlorite production process is used, since an excess of free chlorine will be present. Despite a number of known toxic effects associated with chlorine dioxide and its by-products chlorite and chlorate, none have been apparent in clinical trials. In addition, studies have found no evidence for the mutagenic activity of chlorine dioxide, chlorite or chlorate (Meier *et al*, 1985).

The effects of PAA are difficult to separate from those of hydrogen peroxide, with which it exists in equilibrium. Both PAA and hydrogen peroxide have been shown to exhibit mutagenicity. In addition peracids (and also ozone) have the potential in certain circumstances to produce epoxides by the oxidation of alkenes, which are known to induce a wide range of genetic effects including cancer.

In contrast to other disinfectants, where the generation of micropollutants is of most concern, the Clariflow process produces a bulk by-product (lime-sludge) which required disposal. Although less hazardous, this has significant economic implications. The Clariflow process could affect the localised receiving environment through the discharge of a high pH effluent, however this was not observed during operation at Sandown.

Due to the lack of long term operation of any of the disinfection processes other than chlorine, evaluation of their hazardous effects remains largely unresolved. However, whilst the absence of any deleterious effects seems unlikely, it would seem that the environmental impact of disinfectants such as ozone and UV will be of a lesser magnitude than that arising from the use of chlorine compounds.

12. WATER AUTHORITY ATTITUDES TO DISINFECTION OF MARINE DISCHARGES

During the course of the study, water authorities were consulted with regard to current policy and attitudes to disinfection of marine discharges. Discussions were held with officers and the reports given below represent the opinions of the officers rather than the Authorities' formal position. A summary of disinfection trials carried out by various authorities is presented in Table 12.1.

12.1 Anglian Water

Anglian Water considered disinfection options in 1986-7 and undertook small batch scale trials on ozone with some success. Planned larger scale through-flow ozonation studies were later cancelled. Trials were undertaken with PAA in 1987 and data from the trials are currently being prepared as an internal report. Anglian Water are concerned over the efficacy of disinfection, particularly in relation to potential impact on shellfisheries; there are four designated shellfisheries at Colchester alone. Due to this concern, and the high operating costs, research and development into disinfection has effectively been terminated. The overall policy is to opt for properly designed and constructed, dispersive, long sea outfalls.

Aspects identified as requiring research were the validity of indicator organisms, and efficiencies of the processes when used on site. Clarification was also sought regarding bathing water compliance under abnormal weather conditions.

12.2 North West Water

North West Water undertook chlorination trials at Blackpool approximately five years ago. A review was made of disinfection options in 1988 in relation to the Fylde Coast; the conclusion was that disinfection was a non-viable option because of the size of

Table 12.1: Summary of Water Authority pilot wastewater disinfection trials

Water Authority	Chlorine (ICI)	Sodium Hypochlorite (ICI)	Ozone (Ozotech)	UV (Hanovia)	Clariflow (Blue Circle)	PAA (Interox)
Anglian			Clacton (1986)			Clacton and Southend (1987)
North West		Blackpool (1983)				
Southern+		Barton-on-Sea (1984)			Sandown* (1984-date)	
South West		St.Agnes (1987)		Par and Ladock (1987)		Plymouth (1987)
Welsh	Pwll (1978)	Bishopston (1979)				Bishopston (1979)
Wessex	Weston-S-Mare* (1976-1983)	Weston-S-Mare* (1983-date)				Weston-S-Mare (1987)

* Full scale operation

\+ A full scale OSEC plant at Portsmouth was abandoned.

the scheme and the lack of existing demonstration plants. A long sea outfall was therefore the preferred option.

Failure to achieve EEC standards at other coastal areas is thought to relate to river discharges, and it is intended to investigate the source(s) of bacterial pollution more fully. There are no plans for disinfection of effluents from inland works, or for long term disinfection of marine discharges, although it may be used as an interim measure pending engineering solutions.

12.3 Southern Water

Southern Water undertook hypochlorite trials at Barton-on-Sea in 1984, but did not proceed further because of cost considerations, and doubt as to whether exceedance of EEC standards at beaches further along the coast occurred entirely as a result of the Barton-on-Sea discharge. More recently, the lime based Clariflow process has been in operation at Sandown on the Isle of Wight. Operated to date by the manufacturers, the plant has been successful, but Southern Water are keen to investigate disinfection efficacy at pH levels lower than the current operating pH of 11. Overall, Southern Water's policy is to use long sea outfalls wherever possible and their programme in this respect is perhaps the most advanced.

12.4 South West Water

South West Water are actively considering disinfection. The overall policy presently under consideration is to have long sea outfalls, possibly with disinfection as an interim measure during construction in certain instances, or later as a back-up measure to cope with any future increase in bathing water quality standards.

It is understood that South West Water intend that disinfection will be used on the Mounts Bay outfall for approximately four years while the Penzance/St. Ives outfall scheme is undertaken. Sewage from Penzance and surrounding areas is to be pumped north to a long outfall at St. Ives where the high energy of the sea gives good dispersion. Present discharges to Mounts Bay recirculate due to the prevailing currents and cause contamination of beaches.

South West Water have conducted trials in association with manufacturers on hypochlorite, UV and PAA. PAA and UV are under consideration for further application; irradiation is also considered to be a promising experimental technique but with obvious problems of public acceptability.

12.5 Thames Water

Thames Water have no marine outfalls, but have investigated ozonation for disinfection of inland works effluent discharging to recreational water. It was concluded that ozonation was too expensive to be viable and recreational activities were consequently restricted to those appropriate for the degree of self-purification of the effluent.

12.6 Welsh Water

Welsh Water do not consider disinfection to be a viable option largely because of the potential for ecological-effects, which they do not consider have been adequately addressed as yet. Trials were carried out in 1978-79 on a range of disinfectants including chlorine, chlorine dioxide and PAA. Chlorination was observed to cause significant bioaccumulation of halogenated organics in intertidal organisms, which declined after termination of the trial. On this basis, chlorination was discounted. Biological effects of PAA were not assessed but it was considered that peroxylated by-products such as epoxides may constitute a similar risk to chlorination by-products.

There is concern that disinfection to safeguard health may transfer the problem from public health risk to one of adverse environmental impact. Overall policy is therefore to use long outfalls. Tenby outfall has given good bacterial reductions, while virus numbers in both water and sediments appear to be decreasing with time.

Suggested area of research include:

a) Further field trials on chlorination and alternatives such as ozone and UV, particularly looking at kill in the outfall pipe with extrapolation to bathing beach, rather than vice versa.

b) Monitoring of environmental impact *in situ* (black box approach to determine eg. effects of by-product accumulation in indicator organisms).

c) Epidemiological studies to determine effects of disinfection and/or long outfalls. (Welsh Water have recently submitted proposal to Welsh DoE on this subject, in conjunction with WRc).

d) Use of direct viral enumeration rather than indicators, and assessment of inactivation efficiency for additional viruses such as Norwalk and rotavirus.

12.7 Wessex Water

Wessex Water are the only authority with long term operating experience of wastewater disinfection. Chlorination was initiated at Weston-Super-Mare in 1976, initially intended only as an interim measure. In 1983, the system was converted to hypochlorite for safety reasons. Due to problems in achieving EEC standards (thought to be partly due to encapsulation effects), high chlorine doses are used giving residuals of between 25-45 mgl^{-1}. Pressure for compliance with EEC standards appears to outweigh consideration of the possible environmental effects of such high residuals although there are no commercial fisheries or shellfisheries in the area.

The possible need to convert to an alternative system, however, prompted trials with PAA in 1986, but due to operational problems with manufacturers dosing equipment, the results were largely inconclusive. Current modifications to improve disinfection efficiency include the construction of large contact tanks, which will increase contact time and provide for some stormwater balancing. It is understood that if these modifications fail to achieve compliance, the option of a long sea outfall will again be investigated.

12.8 Yorkshire Water

Yorkshire Water have no operational disinfection systems nor have any under development.

12.9 Conclusions

The general concensus among water authorities would appear to be to opt for long sea outfalls wherever possible. Even with adequate screening and disinfection, the public acceptability of swimming in sewage polluted waters is questioned. Although there is a great deal of interest in the potential for disinfection, there is a general reluctance for its adoption on a long-term basis because of the lack of proven efficacy and the high operating costs. The awareness of environmental impact observed by water authorities, both in-house and increasingly amongst consumers, also tends to mitigate against disinfection. It is however being seriously considered, as for example by South West Water, as a short term measure while outfalls are constructed.

13 DISCUSSION AND CONCLUSIONS

In considering the choice of disinfectant, the knowledge of its inactivation of pathogenic microorganisms as well as indicator species is necessary. A disinfectant may permit the achievement of compliance with EEC coliform standards, but will not necessarily safeguard public health as a result. Comparison of the relative resistance of different groups of organisms to alternative disinfectants indicates that in nearly every case, resistance follows the series;

bacteria < viruses < bacterial spores < protozoan cysts

Bacteria are generally the most susceptible group. Viruses tend to be more resistant than bacteria because they are smaller and gain greater protection through encapsulation in solids; outside the host cell they have no metabolism as such, therefore unlike bacteria, they are immune to metabolic interference. Spores and cysts are physiological adaptions for survival in unfavourable conditions and as such would be expected to confer a high resistance to chemical attack.

Resistance also varies within each group; for example it would appear that coliforms frequently exhibit less resistance to disinfection than faecal streptococci and some species of *Salmonella*. In very broad terms, disinfection requirements could thus be regarded as being lowest for the indicator group. If disinfection is applied to achieve compliance with EEC standards, there will be an advantage in using those disinfectants which achieve a greater kill of other microorganisms at a similar dose rate. Ratios of Ct values for viruses, spores and cysts to those of coliforms for a range of disinfectants were given in Figure 11.1 (Section 11.1). These suggested that ozone, UV and radiation will give a greater incidental removal of pathogens when dosing to achieve compliance with coliform standards only. Chlorine and PAA however, require proportionately higher Ct values to achieve a broad spectrum kill.

Information reviewed in the preceding sections of the report has indicated that there is probably not a single disinfectant which is preferable for wastewater treatment, but that the choice will be largely site-specific. Important considerations include the size of installation, the nature of the effluent and the effluent discharge quality requirement. Economies of scale are observed with eg. chlorine, whereas operating costs for UV increase proportionately with flow; the latter is thus more suited to smaller installations. For crude sewage, the disinfectants which are adversely affected by the presence of solids, ie ozone and UV, would not act effectively, whereas chlorine or chlorine dioxide would be appropriate. Compliance with EEC coliform standards could most expediently be achieved with chlorine, whereas a requirement for, eg., enhanced viral removal would lead to the use of ozone or chlorine dioxide in preference to chlorine. The more stringent the effluent discharge requirements, the more feasible alternative systems such as ozone and UV become. A summary of the factors affecting the applicability of both operational and experimental disinfection systems is given in Tables 13.1 and 13.2.

Consideration of safety aspects in heavily populated coastal areas would tend to mitigate against the use of liquid chlorine, bromine chloride, chlorine dioxide and radiation. Since 1982, HSE regulations have required that storage of over 10 tonnes of liquid chlorine be licensed, which has acted as a disincentive for its use. Safety considerations led Wessex Water to convert from chlorine to hypochlorite at Weston-Super-Mare. Similar storage hazards would pertain to the use of bromine chloride. Other disinfectants which are generated on demand do not present an attendant public risk from bulk transport and storage, although chlorine dioxide has a high explosive potential. New techniques for its generation under vacuum have, however, recently reduced this risk. Ozone and UV are only likely to be hazardous to operators; with sophisticated ozone leak detectors, the chance for

Table 13.1: Summary of operational wastewater disinfection techniques

	Chlorine Gas	Sodium Hypochlorite	OSEC	Ozone	UV	Clariflow
Bactericidal	good	good	good	good	good	good
Virucidal	poor	poor	poor	good	good	good?
Regrowth	yes	yes	yes	no	yes	no
Fish toxicity	toxic	toxic	toxic	none expected	non-toxic	localised
Hazardous by-products	yes	yes	yes	minimal	no	sludge
Corrosive	yes	yes	yes	yes	no	no
Community safety risks	yes	no	no	no	no	no
Operator safety risks	high	moderate	moderate	moderate	low	low
Transportation	substantial	substantial	no	no	no	sludge disposal
Relative complexity of technology	simple - moderate	simple	moderate	complex	simple - moderate	moderate - complex
Process control	well developed	well developed	developing	developing	developing	developing
Equipment reliability	good	good	fair-good	fair	fair	?
Size of plant	all sizes	all sizes	small - medium	medium - large	small - medium	small - medium
Pretreatment required	none	none	none	secondary	secondary	none
O + M sensitive	minimal	minimal	high/ moderate	high	moderate	high/ moderate
Total costs	low	low	moderate	high	moderate	high

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Table 13.2: Summary of experimental wastewater disinfection techniques.

	Chlorine dioxide	PAA	Bromine-chloride	Irradiation
Bactericidal	good	good	good	good
Virucidal	good	poor	fair-good	good
Fish toxicity	toxic	toxic	moderate	?
Hazardous by-products	some	?	yes	?
Corrosive	yes	yes	yes	no
Community safety risk	no	no	yes	yes
Operator safety risk	high	moderate	high	high
Transportation	no	substantial	substantial	yes
Relative complexity of technology	moderate	simple	moderate	complex
Process control	no experience	developing	developing	developing
Size of plant	medium-large	all sizes	all sizes	?
Pretreatment required	none	none	none	none
O + M Sensitive	high	high	high	high
Total costs	moderate	moderate	moderate	high

leakage of ozone outside the generation building would appear to be low. Radiation hazards are not easily quantifiable. A major factor mitigating against the use of radiation may be public acceptability, although if food irradiation (currently used in over thirty countries) is adopted in the near future, this aspect may decline in significance.

Purely on an economic basis, the case studies presented in Section 11.2 and summarised in Table 13.3 show that total costs for crude sewage disinfection increase according to the following series:

Cl_2(gas) < Cl_2(hypo) < Cl_2(OSEC), PAA < Clariflow

Estimated costs for the disinfection of secondary effluent compare as follows:

Cl_2(gas) < Cl_2(hypo) < Cl_2(OSEC) < UV, PAA < O_3

However, the budget estimates given are subject to a wide range of variables, from effluent quality to the state of the market. Large scale adoption of any one system in the UK could result in significant price reductions. A monopoly over equipment or chemicals may give rise to a user's concern over future pricing policy.

On the basis both of cost and familiarity with existing technology, chlorine appears the most widely applicable disinfectant. However, its environmental impact is significant. The work by Welsh Water has demonstrated that bioaccumulation of halogenated by-products can occur as a result of wastewater chlorination. Although no deterious effects as such were observed during the course of that short study, there is sufficient concern over build-up in the marine biota of anthropogenic compounds already present in wastewaters (as evidenced by debate at the 1987 North Sea Conference) perhaps to warrant avoiding a deliberate increase in micropollutant loading. However, the potential for dissipation of

Table 13.3: Summary of estimated total treatment costs (1988) for hypothetical UK application of disinfection processes

Disinfection process	Total cost (pm^{-3})[1]			
	Screened raw sewage		Biologically treated sewage	
	6 month operation	12 month operation	6 month operation	12 month operation
gaseous chlorine[2]	2.0-5.5[3]	1.6-5.1	(1.4)[4]	(1.1)
hypochlorite solution[2]	2.1-7.0	1.7-6.6	(1.5)	(1.2)
on-site electrolytic chlorination	3.8-15.2	2.4-9.6	(2.6)	(1.6)
ozone	no data assume=20	no data assume=13	12.8	7.3
ultraviolet irradiation	not appropriate	not appropriate	4.9	3.5
peracetic acid	11.6	10.9	(4.0)	(3.5)
Clariflow[5]	26.9	18.5	not appropriate	not appropriate

[1] based on 1988 prices - includes amortised capital costs (as discussed in text) and full operation and maintenance

[2] if dechlorination using sulphur dioxide was adopted, costs could increase by approximately one third

[3] range of costs based on low (20 mgl^{-1})and high (100 mgl^{-1}) dosages

[4] figures in parentheses are approximate estimates for low dosages extrapolated from raw sewage applications

[5] costs influenced significantly by local sludge disposal situation

accumulated contaminants after termination of chlorination, demonstrated in the Welsh Water study, suggests that seasonal disinfection may have less impact than year-round disinfection, by permitting an intermittent "recovery" period.

The major UK suppliers of hypochlorite (ICI) consider that the size of the market in wastewater disinfection cannot support large scale research into its environmental impact. It is indicated in publicity material that "although chlorinated hydrocarbons may be found in minute quantities following the use of sodium hypochlorite, there is no evidence of any environmental or health impact given the minute quantities and the massive dilution which takes place in the sea. When used correctly, there is no evidence of adverse effects on fish stocks." That there is no evidence of adverse effects rather than evidence of no adverse effects may be significant. In this respect, further investigation of any effects observed at US installations (where chlorination has been practised for up to 50 years but is coming under increasing scrutiny with regard to environmental impact) would seem beneficial.

Much attention in the US is focussed on the residual toxicity of chlorinated effluents. A maximum discharge limit of 1.5 mgl^{-1} total residual chlorine is stipulated in Massachusetts, whereas in California, where water reuse is widespread, effluent discharged to enclosed bays and estuaries must not contain material toxic to biota. This has led to adoption of dechlorination and alternative disinfectants. Effluent discharged to sea cannot exceed a six month median total chlorine residual of 0.002 mgl^{-1}; a daily maximum of 0.011 mgl^{-1} or an instantaneous maximum of 0.126 mgl^{-1}. The high detection limits for residual chlorine compared to the low biological effect level mean that monitoring is difficult. Nevertheless, the degree of concern and hence the stringency of limits applied in US states contrasts with the residual chlorine concentrations of 25-45 mgl^{-1} in effluent discharged at Weston-Super-Mare.

Preliminary studies at Plymouth Marine Laboratories have indicated that the residual toxicity of PAA may be comparable to that of chlorine, both compounds giving similar acute toxicity curves. There is also concern over the mutagenic properties of the equilibrium components of the peroxygen disinfectant, ie. acetic acid and hydrogen peroxide. Mutagenic or genotoxic potential is also implicated to varying degrees with the use of other halogens eg. bromine chloride, chlorine dioxide, and with ozone and irradiation. Disinfectants may generate residuals or by-products which cause direct mutagenicity in marine organisms, or by permitting accumulation of contaminants in shellfish, could cause mutagenicity in consumers. Where accumulation of contaminants in marine organisms does not give rise to direct adverse effects, there may be associated impacts such as reduced resistance to eg. viral infections. Viruses may put promoters upstream and this can lead to tumour formation; this might happen in shellfish but has yet to be described. However, viable filter-feeding shellfish may also accumulate viruses directly and this has led to food poisoning. In the extreme, it could be said that the mutagenic effects of disinfection on viruses could theoretically produce a worse infective virus than those currently known.

In considering the possible effects of disinfectant by-products, however, it should be borne in mind that many of the compounds concerned occur naturally in the marine environment, for example peroxidase organisms produce hydrogen peroxide in nmol l^{-1} concentrations, which is consumed in the degradation of organic matter. Similarly, THMs such as chloroform and bromoform occur naturally in the sea at the ugl^{-1} level. Risk assessment of disinfectant by-products must maintain a perspective with regard to the concentrations which are likely to occur near outfalls. The potential for mutagenic and genotoxic effects of disinfectants and their by-products must also be looked at in context; many compounds can be shown to cause mutagenic effects when applied at high concentrations, but it is necessary to know whether they will do so at probable ambient concentrations. Whether levels likely to occur near outfalls can be classified as significant in terms of adverse environmental impact is difficult, if not impossible, to assess with the current paucity of data.

Sewage disinfection would not necessarily be the sole source of hazardous by-products. For example, chlorinated cooling water from coastal power stations may represent a significant input. A calculation of consumption of household bleach, based on annual market figures, suggests that this source alone could provide a typical chlorine concentration in domestic wastewater of 5 mgl^{-1}. In terms of direct human risk, it could be argued that the frequency and magnitude of exposure of swimmers to chlorinated compounds would probably be much higher in heavily chlorinated municipal baths than in seawater.

Nonetheless, disinfectants are by their very nature harmful to biological systems. Expectation that an agent can be identified which can achieve 100% kill at one end of an outfall pipe and have zero effect at the other end may be optimistic. Of the available alternatives, UV appears to come closest to achieving this but is only fully effective on a effluent containing few suspended solids (eg treated effluent). On the basis of environmental impact alone, the option of a long sea outfall would seem preferable. Long sea outfalls form the option largely chosen by Water Authorities. Before the alternative of disinfection can be applied with reasonable assurance, there are a number of areas which require clarification.

It is considered that **there are insufficient field trial data on the efficiency of alternative disinfectants.** A review of operational experience in the US, where disinfection of wastewaters is widely practised, may prove valuable particularly in relation to marine discharges. In the UK, field trials of longer duration are required to give performance data under a range of weather conditions and to assess potential environmental impacts more thoroughly. Testing for specific inactivation efficiency should be carried out in or at the outfall, since beach sampling may be affected by other diffuse discharges or resuspension from sediments. Work which has been carried out in the UK has not in all cases been widely publicised; it would seem that a form of round-tabling of interested individuals from Water Authorities with DoE would be of benefit in this respect.

A further observation is that **there are insufficient field trial data on the efficiency of different disinfectants for organisms other than coliforms.** Viruses in particular are highlighted as a group of increasing significance. It could be speculated that with growing awareness of the health threat posed by viruses (not only gastroenteritis associated with rotavirus, adenovirus, small round viruses of various types and Norwalk virus but from others such as Hepatitis A virus), any future revision of water quality standards may be directed towards this aspect in particular. The risk from viral infection as compared to bacterial infection is enhanced by the capacity for prolonged viral survival in sediments, combined with the low infective dose required. The implications of seasonal disinfection, whereby accumulation of pathogens in sediment reservoirs could occur during non-disinfection periods, and the possible re-release of sediment-harboured microorganisms are as yet unknown.

Associated with this is the question of **identification of appropriate viral indicators**, to ensure that receiving bathing waters, while complying with coliform standards, do not pose a serious threat from other organisms. Faecal streptococci are considered to represent a better indicator for viruses than coliforms, and coliphages better than faecal streptococci. It may be more useful in the long term to direct research efforts towards producing a technique for direct viral enumeration, rather than identifying indicators. One such that has been developed commercially in the US is the gene probe.

A gene probe is a radio- or enzyme-labelled single strand of nucleic acid which is complementary to the viral nucleic acid. If the gene probe binds to nucleic acid on addition to an extracted, filtered sample, the presence of the target virus is indicated. Gene probes have been developed for different types of virus but it is understood that, since enteroviruses exhibit a degree of homology in the earlier parts of the nucleic acid, it may be possible to develop a probe to indicate the group as a whole. Although this approach would be quicker and cheaper than conventional assay techniques (the US version is reported to take one day and costs $50 per kit) and would avoid the problems of sample toxicity to assay cells which occurs with contaminated water, it would seem to have a significant drawback. Since the viral nucleic acids have to be extracted before testing, it is not evident from the result whether or not the the virus was originally viable. For disinfectants which inactivate viruses by damaging the capsid but leaving the nucleic acid intact, a gene probe may give an underestimation of efficiency.

The problem of determining viability is particularly pertinent to sewage disinfection. **It is necessary to determine whether reported inactivation efficiencies of alternative disinfectants could be influenced by the phenomenon of viable, non-culturable cells.** Well documented work by Rita Colwell at the University of Maryland, and others, has demonstrated that pathogenic bacteria can be present in marine waters, yet remain undetected when water samples are tested using conventional plating methods.

Recent work at the University of Newcastle Upon Tyne has indicated that, as determined by conventional methods, bacterial numbers decline steadily with distance from an outfall such that the majority of *E coli* are non-culturable within ten days, but that cell integrity, as observed with fluorescence microscopy, is maintained. This effect has been observed elsewhere for *E coli, Vibrio cholerae* and *Salmonella enteridis*, and non-culturable cells have been shown to remain virulent in animal studies. It is thought that under nutrient-poor conditions (such as in seawater) cells can exist in a dormant or semi-spore like state, from which they can recover both in terms of culturability and virulence when returned to favourable conditions. Assessment of the performance of disinfectants by beach sampling rather than at the discharge point may therefore give an underestimation of the potential health risk.

Aspects of health risks, both indirect to humans and direct to the marine biota in receiving waters, suggest strongly that **trials need to be undertaken to evaluate the environmental impact of disinfectant residuals and by-products.** This is perhaps of most significance for chlorine and PAA, which may be the options most likely to be taken up in the short term. The generally increased level of concern over chlorination side-effects prompts the use of alternatives like PAA. However, large scale adoption of this or other alternatives in preference to chlorine may be premature, since their environmental impact has not yet been adequately assessed.

In conclusion, there are several processes available which can disinfect sewage to achieve coliform levels permitting discharge through comparatively short outfalls. Estimates of UK costs show prices ranging from approximately 1.6 pm^{-3} to 19 pm^{-3} for year-round disinfection or 2.0 pm^{-3} to 27 pm^{-3} for six monthly operation (Table 13.3). These costs would reduce slightly for very large outfall schemes, and in some cases such as Clariflow, are associated with additional benefits such as increased BOD, SS and heavy metal removal. In this respect (although not included in the present remit), it would be of interest to compare the costs of disinfection options with those for a long sea outfall. The figures presented should also be viewed in the context of the costs levied by Water Authorities for full biological treatment for subsequent discharge to an inland watercourse, typically 25 pm^{-3}. In relation to this, those processes at the lower end of the cost range indicated may be attractive if they can be shown to be environmentally acceptable.

A major drawback with disinfectants is the formation of hazardous by-products. It is difficult to interpret existing information in the context of the marine environment rather than in relation to human consumption, since much of the toxicological data for chlorinated by-products relates to exposure via drinking water. The processes with the least by-products are either very costly or not presently effective for raw sewage. The only option without associated by-products is a long sea outfall. Until further evidence proves otherwise, it is considered that disinfection by chemical means should only be used on a short term basis, while an outfall is being constructed. It is interesting to note the apparent recovery of marine organisms from the effects of chlorinated discharge in the Welsh Water study; this suggests that seasonal disinfection may be less environmentally detrimental than year-round treatment.

Where standards are imposed rigorously and beaches have to remain open for five years or so until an outfall scheme (or land-based treatment) comes on-stream, a choice of disinfectant may well have to be made. If economic considerations prevail, chlorine compounds (specifically hypochlorite) are attractive. Seasonal application and dechlorination to preclude residual toxicity could be used to reduce environmental impact. However, experience at Weston-Super-Mare, where dosages at the upper end of the chlorine range in Table 13.3 are applied and compliance is still not always achieved, has to be borne in mind. Although from approximately three times more expensive than gaseous chlorine, the lower degree of by-product formation associated with chlorine dioxide suggests that it merits further investigation as a wastewater disinfectant.

If economic aspects are not overriding and minimal environmmental impact is considered important, the Clariflow process could have application. However, construction time, land acquisition, sludge disposal and an overall cost approaching that of land-based treatment would have to be considered. Ozone is a potentially attractive option in economic comparison to Clariflow, but its efficacy on crude sewage is not well documented. The intermediate option in terms of both cost and likely impact is PAA, however it is not possible to assess the latter factor adequately on the basis of current data.

An examination of embryonic technologies for sewage disinfection identified no systems which showed sufficient development potential for use within the next five years.

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Appendix I

CHLORINE GAS (PORTACEL)

Portacel Limited, a subsidiary of Portals Water Treatment Limited, market a range of gas chlorination equipment and have commissioned chlorination plants for water authorities, industrial process waters, cooling systems as well as for effluent treatment. Portacel manufacture gas chlorinators which incorporate vaccum chlorine regulators. These are widely considered to be inherently safer than pressure chlorinators as the occurrence of a leakage draws in air and prevents gas escaping. A changeover device is provided to ensure continuity of supply.

Basis for design

Chlorine is suitable for disinfecting sewage which has undergone preliminary treatment only. A dose of 20 mgl^{-1} was considered to achieve adequate disinfection, based on operational data from wastewater chlorination plants in the US. A higher dose of 100 mgl^{-1} was included in consideration of the trials at Weston-Super-Mare. The costs for the higher dose were obtained by adjusting the chemical costs only as the capital costs were assumed not to change significantly.

The required capacity of the unit would be approximately $25kgh^{-1}$. For this application continuous withdrawal from 844kg drums is recommended, and would require 3 such containers at a withdrawal rate of approximately up to 9 kgh^{-1} at 15°C with 3 additional drums in reserve to be brought into service automatically when the duty supply becomes exhausted. Though the budget costs include an automatic changeover device, this could be carried out manually with a substantial saving in capital costs (at the expense of operating costs and personnel safety). The gas would then pass to 2 vacuum regulators (1 per chlorinator) where the gas would be reduced to a pressure less than atmospheric before being conducted to 2 Chlorine metering pumps (1 as standby) and thence to the water operated ejectors. Each ejector would be driven by a booster pump drawing its supply from the effluent or a convenient source.

Power costs for the plant are estimated at 3.5kWh assuming one booster pump and one chlorinator running at the same time. Assuming separate drum storage and plant rooms averaging 5mx5mx4m high and 5mx5mx3m high respectively, heating requirements are estimated at 8kWh for 3 months of the year; lighting would be approximately 1kWh.

Capital Costs

1 X Chlorine gas header to accommodate two banks of three drums.

1 X Chlorine gas changeover device.

2 X Vacuum regulators.

2 X Automatic wall mounting chlorinators, (one standby), arranged for automatic control from a 4-20 mA linear to flow signal and each complete with ejector and vacuum status switch to indicate failure of gas or injector water supply.

2 X Booster pumps (one standby).

1 X 10m run of 2" solution delivery pipework.

1 X 6m run 3/4" injector vacuum tubing.

1 X 6m run of 2" pump suction and delivery pipework.

1 X Series 65 chlorine leak detector.

1 X Combined drum lifting beam/weigher.

1 X Manually operated travelling hoist.

6 X Sets of four drum rollers.

1 X Life support air breathing set.

1 X Alarm panel.

1) Equipment cost		
£23000 +15% design and supervision	£26450	
2) Amortised equipment cost (9% over 15 years)		£3281 y^{-1}
3) Civil cost		
a) 40m^2 of buildings for plant room and drum room at £600 m^{-2} for a serviced building to safety standard	£24000	
b) Contact tank: 30 min @ 3DWF		
i.e. $\frac{1}{2} \times \frac{1}{24} \times (3 \times 4500)\ m^3$		
= 281.25 say 300 m^3* @ £150 m^{-3}	£45000	
(* could be provided possibly as a large culvert)		
c) Design and supervision	£10350	
	£79350	
4) Amortised civil cost (9% over 40 years)		£7376 y^{-1}
5) Total capital cost (1 + 3)	£105800	
6) Total amortised capital cost (2 + 4)		£10657 y^{-1}
7) Amortised capital cost (pm^{-3})		
i) Based on 1.5 DWF for 6 months		
$1.5 \times 4500 \times 182.5 = 1.232 \times 10^6\ m^3y^{-1}$		0.87 pm^{-3}
ii) Based on 1.5 DWF for 12 months		
$1.5 \times 4500 \times 365 = 2.464 \times 10^6\ m^3y^{-1}$		0.43 pm^{-3}

Operation and Maintenance Costs

8) Chemical

(a 20mgl^{-1} dose @ £430-450 tonne^{-1}) 0.9 pm^{-3}

(a 100 mgl^{-1} dose @ £430-£450 tonne^{-1}) 4.4 pm^{-3}

9) Power

i) summer

$3.5 \times 24 = 84$ kWhd^{-1}

$+ 1 \times 6 = 6$ kWhd^{-1}

$= 90$ kWhd^{-1} $\times$ 5.5 pd^{-1}

$= 495$ pd^{-1}

for say average flow of 1.5×4500 m^{3}d^{-1}

$= \frac{495}{6750}$ pm^{-3} 0.08 pm^{-3} (summer)

ii) winter

As above plus heating for system in winter (if used)

90kWh + $(8 \times 24) = 282$ kWhd^{-1}

$= \frac{282 \times 5.5}{6750}$ = 0.23 pm^{-3} for 3 months

0.08 pm^{-3} for 9 months 0.12 pm^{-3} (all year)

10) Labour

$2 \times 0.5\text{h} \times 3$ times wk^{-1} = 3 man h

maintenance say 1 hwk^{-1} average = 1 man h

4 hwk^{-1} @ £12 h^{-1}

$\frac{48 \times 100}{7 \times 1.5 \times 4500}$ 0.10 pm^{-3}

11) Spares etc say 2% of equipment y^{-1}

= £460 y^{-1}

i) summer only $\frac{460 \times 100}{1.232\times10^{6}}$ pm^{-3} 0.04 pm^{-3}

ii) all year	$\frac{460 \times 100}{2.464\times10^6}$	pm^{-3}	0.02 pm^{-3}

12) Total operating costs

i)	summer operation only (8+9(i)+10+11(i))	1.12 - 4.62 pm^{-3}
ii)	all year round (8+9(ii)+10+11(ii)0	1.14 - 4.64 pm^{-3}

13) Total overall cost

i)	summer only (7(i)+12(i))	1.99 - 5.49 pm^{-3}
		say 2.0 - 5.5 pm^{-3}
ii)	all year round (7(ii)+12(ii))	1.57 - 5.07 pm^{-3}
		say 1.6 - 5.1 pm^{-3}

SODIUM HYPOCHLORITE: (ICI)

ICI is Britain's main manufacturer of sodium hypochlorite which is produced by a reaction between chlorine gas and caustic soda solution. The minimum storage capacity recommended by ICI is equivalent to one weeks' usage plus the contents of a road tanker. In addition an allowance of 10% free space should be made when calculating the gross capacity. Road tankers carrying 23 tonnes are used for delivering sodium hypochlorite, which together with a weekly usage of 20.6 tonnes hypochlorite (3 tonnes active chlorine) gives a tank size of about 50 tonnes. Basis for design is as for chlorine gas.

Capital Costs

1 X HDPE 50 tonne storage tank

2 X Pumps

1 X Residual chlorine controller

Pipework

1) Equipment costs		
£15000 +15% design and supervision	£17250	
2) Amortised equipment cost (9% over 15 years)		£2140 y^{-1}
3) Civil cost		
Building estimated at 40 m^2	£24000	
Contact tank (as chlorine)	£45000	
Design and supervision	£10350	
	£79350	
4) Amortised civil cost (9% over 40 years)		£7376 y^{-1}

5) Total capital cost (1 + 3)	£96600	
6) Total amortised capital cost (2 + 4)		£9516 y^{-1}
7) Amortised capital cost (pm^{-3})		
i) Based on 1.5 DWF for 6 months (1.232×10^6 m^3y^{-1})		0.77 pm^{-3}
ii) Based on 1.5 DWF for 12 months ($2.464 \times 10^6 m^3y^{-1}$)		0.38 pm^{-3}

Operation and Maintenance costs

8) Chemical (@ 20 mgl^{-1} chlorine (142 mgl^{-1} hypochlorite solution) @ £85 $tonne^{-1}$ (± 20%))		1.2 pm^{-3}
(100 mgl^{-1} chlorine : 714 mgl^{-1} $NaOCl^{-1}$)		6.1 pm^{-3}
9) Power (minimal)	say	0.05 pm^{-3}
10) Labour		0.10 pm^{-3}
11) Spares say 2% of equipment y^{-1}=£300		
i) summer only		0.02 pm^{-3}
ii) all year		0.01 pm^{-3}
12) Total operating costs		
i) summer only (8+9+10+11(i))		1.37 - 6.27 pm^{-3}
ii) all year (8+9+10+11(ii))		1.36 - 6.26 pm^{-3}
13) Total overall cost		
i) summer only (7(i)+12(i))		2.14 - 7.04 pm^{-3}
	say	2.1 - 7.0 pm^{-3}
ii) all year round (7(ii)+12(ii))		1.74 - 6.64 pm^{-3}
	say	1.7 - 6.6 pm^{-3}

OSEC (WALLACE AND TIERNAN)

Wallace and Tiernan manufacture an OSEC system for the generation of chlorine from brine or seawater. Details of the brine system only are presented here. The main components of the OSEC system are - the rectifier/control panel, salt saturator, electrolyser with hydraulic panel and brine pump and product tank. Standard accessories include - hydrogen removal apparatus, water softeners and dosing pumps. Basis for design is as for chlorine. Wallace & Tiernans largest standard modules (B8-200) have a maximum equivalent chlorine capacity of 952 kgd^{-1}. Multiple module arrangements are used for larger capacities. Without any detailed costings of the larger module (of which a minimum of 3 would be required for the higher dosing regime), estimates have been based for the higher dose regime on the B4-200 unit which has a maximum equivalent chlorine capacity of 476 kgd^{-1}. To achieve a dosing capacity of 2100 kgd^{-1}, a minimum of 5 units would be required. Although there is little economy of scale associated with increasing capacity using OSEC, there may be some overlap involved (in pipework, instrumentation etc) and costs have therefore been scaled up by a factor of 4, rather than 5. This would appear a reasonable assumption as the relative costs for chlorine gas and hypochlorite are also a factor of 3-4 times higher for the higher dose regime; although costs for OSEC are likely to rise proportionately more.

Capital Costs

One B4-200 brine OSEC unit suitable for a maximum of 438 kgd^{-1} of equivalent chlorine complete with 368 anodes, 400 cathodes, duty and standby brine pumps complete with pulse dampener, in control cabinet complete with mimic diagram and facilities for changing from duty to standby brine pump and from duty to standby hydrogen blower.

One transformer rectifier giving an output of 3000 amps, 32 volts, DC, from an incoming electricity supply of 380/440 volt, 3 phase, 50 Hz, 4 wire.

One Forbes Ltd. salt saturator with a capacity of 40 tonnes recharge 28 tonnes. Unit 3050 mm ID x 7006 mm high. The saturator gives approximately 30 days salt storage.

One Allibert Helix storage tank constructed in black H.D.P.E. 3084 mm diameter x 7648 mm cylinder height, complete with all necessary ancillary features.

Unit complete with:-

Level sensors
Teestronic liquid level sensor with adaptor
Duty and standby hydrogen blowers
Air flow alarm
Overflow alarm

Tank capacity gives in excess of 20 h sodium hypochlorite storage.

Four Kinetico water softening systems each complete with salt for commissioning and non-return and vacuum breaker valve.

Two, one duty/one standby, duplex sodium hypochlorite dosing pumps. For insertion in the sodium hypochlorite line we include for one back pressure valve, one relief valve, one mains injection fitting, one calibration chamber and one pulse dampener.

One heat exchanger consisting of titanium tubes within RPVC tubes operating from the outlet of the electrolyser and for use if the water temperature to the softeners falls below 12°C.

1) Equipment cost
£150000 + 15% design and supervision £172500

2) Amortised equipment cost (9% over 15 years) £21400 y^{-1}

3) Civil cost

Building 90m^2	£54000
Contact tank as chlorine	£45000
Design and supervision	£15000
	£114000

4) Amortised civil cost (9% over 40 years) £10597 y^{-1}

5) Total capital cost (1 + 3) £286500

6) Total amortised capital cost (2 + 4) £31997 y^{-1}

7) Amortised capital cost (pm^{-3})

i) Based on 1.5 DWF for 6 months (1.232×10^6 m^3) 2.60 pm^{-3}

ii) Based 9oon 1.5 DWF for 12 months (2.464×10^6 m^3) 1.30 pm^{-3}

Operation and Maintenance costs

8) Chemical salt and softener regeneration 0.5 pm^3

9) Power 0.4 pm^3

10) Maintenance, say 20% more than gaseous chlorine 0.12 pm^3

11) Spares 2% of equipment cost £3000 y^{-1}

i) summer only $\frac{3000\text{x}100}{1.232\text{x}10^6}$ 0.24 pm^{-3}

ii) all year round $\frac{3000\text{x}100}{2.464\text{x}10^6}$ 0.12 pm^{-3}

12) Total operating cost

i) summer only (8 + 9 + 10 + 11(i))	1.26 pm^{-3}
ii) all year round (8 + 9 + 10 + 11(ii))	1.14 pm^{-3}

13) Total overall cost

i) summer only(7(i) + 12(i))	3.86 say	3.8 pm^{-3}
@ 100 mgl^{-1} dose		15.2 pm^{-3}
ii) all year round (7(ii) + 12(ii))	2.44 say	2.4 pm^{-3}
@ 100 mgl^{-1} dose		9.6 pm^{-3}

ULTRA-VIOLET (HANOVIA)

Hanovia Ltd produce both medium pressure (high intensity) and low pressure (low intensity) arc tubes used for the treatment of municipal and domestic water supplies in hospitals for renal dialysis fluid preparation, in fish farming and food and beverage production.

Basis for Design

To be economic and give an acceptable maintenance level, an effluent quality of 30/30 is required which is equivalent to a 50-66% (1 cm) UV transmission quality.

To accommodate the 21,000 m^3d^{-1} flow, a UV installation based on 9 sets of 4 medium pressure lamps would be required. The lamps contained in quartz sleeves would have an automatic mechanical wiping mechanism. These would be installed horizontally across a stainless steel square section channel. An existing concrete channel would need breaking into to insert the UN channel, which would need to be under cover for lamp changing with the power supplies housed in a weatherproof building.

Capital Costs

The radiation chamber
Constructed with a 316 stainless steel shell with operating pressures up to 15 bar; a quartz tube mounted axially to isolate the arc tube and a viewing port for the UV monitor.

The arc tube
The medium pressure tube is used for high flow rate systems with a maximum power rating of 2.5kW.

Control systems
Contains the electrical supply for the arc tube and is either a basic set of controls or a full system.

UV monitor

Automatic valve

Solenoid operated valve which shuts off fluid flow in the event of power failure or arc tube failure.

1) Equipment cost

240,000 + 15% design and supervision = £276,000

2) Amortized equipment cost

(9% over 15 years) £34,240y^{-1}

3) Civil cost

$15m^2$ building	10,000
Contact channel	2,000
Design and supervision	3,000
	£ 15,000

4) Amortized civil cost

(9% over 40 years) £ 1,394y^{-1}

5) Total capital cost (1 + 3) = £291,000

6) Total Amortized capital cost (2 + 4) £ 35,634y^{-1}

7) Amortized capital cost pm^{-3}

i) based on 1.5 DWF for 6 months

(1.232×10^6 m^3) 2.89 pm^{-3}

ii) based on 1.5 DWF for 12 months

(2.464×10^6 m^3) 1.45 pm^{-3}

Operation and Maintenance Cost

8) Chemicals - nil

9) Power - $\frac{36 \times 2.1 \times 24 \times 5.5}{1.5 \times 45000}$ 1.48 pm^{-3}

10) Labour
1½ hours wk^{-1} @ £12h^{-1} = £18 0.04 pm^{-3}

11) Spares etc.

i) 6 months operation
36 lamps @ £150 = £5,400 + £600 say £,6,000 = 0.49 pm^{-3}

ii) All year around
72 lamps @ £150 = £10,800 + £1200 say £12,000 = 0.49 pm^{-3}

12) Total operating cost

i) Summer (8 + 9 + 10 + 11 (i)) 2.01 pm^{-3}

ii) All year around (8 + 9 + 10 + 11 (ii)) 2.01 pm^{-3}

13) Total overall cost

i) Summer only (6 months)
7 (i) + 12 (i) = 4.90 say 4.9 pm^{-3}

ii) All year around (12 months)
7 (ii) + 12 (ii) = 3.46 say 3.5 pm^{-3}

OZONE (OZOTECH)

Ozotech are a company of engineers and suppliers for ozone systems and have strong connections with Trailigaz, a leading French ozone manufacturer. Trailigaz manufacture three ozone systems generating ozone from air. Monobloc packaged units have a production capacity of up to 3kg O_3 hr^{-1} manufactured as skid mounted packages complete with high pressure drying system. Modular units are based on the Monobloc ozone production cell but use separate skid packaged air chiller/low pressure dryers. Tonozone systems are used for large scale ozone plants from 3kg ozone hr^{-1} upwards. They use low pressure blowers, individual packaged air chillers, dryers and ozonisers. The choice of ozone unit is dependent on cost, power consumption, standby requirements and the required degree of automation.

Basis for Design

For this study the Tonozone system has been considered which though more expensive than the packaged or modular unit, is the most energy efficient.

To prevent excessive consumption of ozone in oxygen demand reactions, the basis of design is a secondary effluent to achieve the necessary 3-4 log reduction in total coliforms the following dose rates are required.

ozone dose (mgl^{-1})	ozone residual (mgl^{-1})	Log reduction
4-8	0.05-0.14	3
5-12	0.11-0.30	4

Thus for a 21,000 $m^{-3}d^{-1}$ plant this would require 3.5 - 10.5 kg O_3 hr^{-1} whilst a 30,000 m^3d^{-1} plant would require 6 - 15 kg O_3 hr^{-1} production. Based on a plant size of 10 kg O_3 hr^{-1}, equivalent to a dose of 11.4 mgl^{-1} at 21,000 m^3d^{-1} and 8 mgl^{-1} at 30,000 m^3d^{-1}, this is expected to achieve adequate disinfection.

Power is consumed in air preparation, air drying, ozone generation and thermal destruction. Specific power consumption for a 10 kg. hr^{-1} Tonozone system at different ozone production rates was used to provide a weighted production rate and power consumption.

Civil Costs

Based on 2 streams, each to treat a maximum 10,500 m^3d^{-1} with a contact time of 20 minutes.

Civil construction costs

approx £ $\frac{10,500}{15,000}$ x 200,00 = 140,000 say £ 140,000

Ozone plant accommodation

approx £ $\frac{10,500}{15,000}$ x 40,000 = 28,000 say £ 30,000

Capital Costs

A) Using a Tonozone unit

1 X 10kg O_3 h^{-1} Tonozone plant

1) Equipment cost (Based on Tonozone unit)
£1,050,000 + 10% design and supervision £1,155,000

2) Amortized equipment costs
(9% over 15 Years) £143,288y^{-1}

3) Civil cost £170,000 + 15% £ 195,500

4) Amortized civil cost
(9% over 40 years) £18,173y^{-1}

5) Total capital costs (1 + 3)	£1,350,500	
6) Total amortized capital cost (2 + 4)		£161,461y^{-1}

7) Amortized Capital Cost (pm^{-3})

i) Based on 1.5 DWF for 6 months ($1.232 \times 10^6 m^3$)	13.10 pm^{-3}
ii) Based on 1.5 DWF for 12 months ($2.464 \times 10^6 m^3$)	6.55 pm^{-3}

Operation and Maintenance Costs

8) Chemicals - essentially nil

9) Power

10 mg^{-1} @ 1.5 DWF = 67.5 kg O_3d^{-1}

For an overall 5.65kg O_3 h^{-1} production, the weighted power consumption is 128.995 kWh, equivalent to 22.83 kWh kg^{-1} O_3.

$$\frac{67.5 \text{ kg} \times 23 \text{ kWh kg}^{-1} \times 5.5 \text{ p kWh}^{-1}}{6750 \text{ m}^3} = 1.27 \text{ pm}^{-3} \qquad 1.27 \text{ pm}^{-3}$$

10) Labour

Assume 6 manhours wk^{-1}. 0.15 pm^{-3}

11) Spares etc. as capital cost so high, assume spares are only 1% y^{-1} £ 10,500

i) summer only	0.85 pm^{-3}
ii) all year	0.43 pm^{-3}

12) Total operating cost

i) Summer only	(8 + 9 + 10 + 11 (i))	2.27 pm^{-3}
ii) All year round	(8 + 9 + 10 + 11 (ii))	1.85 pm^{-3}

13) Total overall cost

i) Summer only	7 (i) + 12 (i)	15.37 pm^{-3}
ii) All year round	7 (ii) + 12 (ii)	8.4 pm^{-3}

B) Alternatively if a Monobloc Ozone unit was adopted capital cost £800,000 compared to £1,050,000

Amortized capital costs would be

7 (i)*	10.34 pm^{-3}
7 (ii)*	5.17 pm^{-3}

Power consumption less efficient (29.5 kWh kg^{-1} vs 23 kWh kg^{-1} but spares slightly less, therefore

12 (i)	2.43 p
12 (ii)	2.11 pm^{-3}

Total overall cost plus

13 (i)	12.77 pm^{-3}
13 (ii)	7.28 pm^{-3}

For ozone: Adopt	12.8 pm^{-3}	summer only
	7.3 pm^{-3}	all year round

CLARIFLOW (BLUE CIRCLE)

Blue Circle Industries plc developed the Clariflow process in conjunction with Southern Water and Portsmouth Ploytechnic. An operational plant at Sandown, Isle of Wight was used as the basis for the case study and costs reported in the literature have been used. The Clariflow process is suitable for raw screened sewage.

Capital Costs

The capital costs at Sandown included the inlay works, sludge handling system etc were approximately £2.4M. For 21,000 m^3d^{-1} Blue Circle estimate revised capital costs may be approximately £1.8M (ie 4 modules at about £450,000).

1) Equipment Cost (estimated)

1) £600,000 + 10% design and supervision
£660,000

2) Amortised equipment cost (9% over 15 years) £81,879 y^{-1}

3) Civil cost

Assume £1,200,000 + 10% design and supervision
£1,320,000

4) Amortised civil cost (9% over 40 years) £122,706 y^{-1}

5) Total capital cost (1+3) £1.980,000*

6) Total amortised capital cost (2+4) £204,585 y^{-1}

*Does not include land value

7)	Amortised capital cost (pm^{-3})	
	i) Based on 1.5 DWF for 6 months ($1.232 \times 10^6m^3$)	$16.6pm^{-3}$
	ii) Based on all year round ($2.464 \times 10^6m^3$)	$8.4pm^{-3}$

Operation and Maintenance Costs

8)	Chemical	
	Assume dose 0.6-0.7 mll^{-1} @ £75 m^{-3}	$5.0pm^{-3}$
9)	Power	
	@ 5.5 $pkWh^{-1}$	$0.67pm^{-3}$
10)	Labour	
	Estimated 60-70 hwk^{-1} @ £12h^{-1}	$1.65pm^{-3}$
11)	Spares etc, say 1% of £600,000	
	i) Summer only	0.49pm-3
	ii) All year	$0.25pm^{-3}$
12)	Sludge disposal	
	Highly dependent on local situation	$2.5pm^{-3}$
13)	Total operating costs	

	i) Summer operation only (8+9+10+11(i)+12)	10.31pm^{-3}
	ii) All year round (8+9+10+11(ii)+12)	10.07pm^{-3}
14)	Total overall cost	
	i) Summer only (7(i) + 13(i))	26.9pm^{-3}
	ii) All year round (7(ii) + 13(ii))	18.5pm^{-3}

PERACETIC ACID (INTEROX)

Interox are the sole UK suppliers of peracetic acid which they manufacture under the trade names Proxitane and Oxymaster. Oxymaster is the range of disinfectants for the disinfection of sewage and sewage effluents.

Basis for design

Oxymaster (12 w/w PAA) would be delivered on site in an 18 tonne bulk tanker and transferred to the site storage vessel by means of SS centrifugal pump which would discharge via SS piping. Storage on site, within a 25 tonne SS vertical cylindrical storage tank equipped with all connections, manways, vents and instruments. Oxymaster would be drawn from the storage tanks by pumps with 316 SS metal and PTFE components. the pipework.valves and contact instruments woulk all be in 316 SS.

Assuming a 15 mgl^{-1} PAA (125 mgl^{-1}Oxymaster) dose will achieve adequate disinfection then a average flow of 1.5 x 4500 = 6750 m^{3}d^{-1} requires 844 kgd^{-1} (max dose 2635 kgd^{-1}).

Capital costs

storage tanks (25 tonne S.S)
dosing pumps
data loggers
on-line monitoring facilities

Total cost £ 83,500

1) Equipment Cost

£ 83,500 + 15% design and supervision £ 96,020

2) Amortized equipment (9% over 15 years)		£ 11,912y^{-1}
3) Civil Cost		
i) Building 40 m^2	£ 24,000	
ii) Contact tank 10 min @ 3DWF = 100 m^3	£ 15,000	
iii) Design and supervision	£ 5,850	
		£ 44,850
4) Amortized civil cost (9% over 40 years)		£ 4,169y^{-1}
5) Total capital cost (1 + 3) =	£140,870	
6) Total amortized cost (2 + 4)		£ 16,081y^{-1}
7) Amortized capital cost pm^{-3}		
i) Based on 1.5 DWF for 6 months (1.232×10^6 m^3)		1.30 pm^{-3}
ii) Based on 1.5 DWF for 12 months (2.469×10^6 m^3)		0.65 pm^{-3}

Operation and Maintenance Costs

8) Chemical	
@ 15 mg/l PAA (ie. 125 mgl^{-1} Oxymaster) £800 $tonne^{-1}$ Oxymaster	10.00 pm^{-3}

9) Power

3 kWh for pumps, light, monitors etc.
@ 5.5p kWh^{-1} based on 1.5 x 4500 m^{3}d^{-1} 0.06 pm^{-3}

10) Labour

4 man hwk^{-1} @ £12h^{-1} to incl. ops. 0.10 pm^{-3}

11) Spares etc. @ 2% of equipment cost £ 1,670y^{-1}

i) Summer only (1.232 x 10^6 m^3) 0.07 pm^{-3}

ii) All year (2.464 x 10^6 m^3) 0.07 pm^{-3}

12) Total operating cost

i) Summer only (8 + 9 + 10 + 11 (i)) = 10.30 pm^{-3}

ii) All year around (8 + 9 + 10 + 11 (ii)) = 10.23 pm^{-3}

13) Total overall cost

i) Summer only (6 months) 7 (i) + 12 (i) = 11.6 pm^{-3}

ii) All year around (12 months) 7 (ii) + 12 (ii) = 10.9 pm^{-3}