# PAPER 8

# Sewage Treatment Processes-the Solution to the Middle East Odour Problem

by

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#### INTRODUCTION

Sewage-treatment processes are by nature offensive, even in countries with temperate climates. In hot climates odour problems are far more serious since high ambient temperatures and long retention times result in the sewage becoming anaerobic very quickly. These conditions also present serious operating problems for both mechanical and electrical equipment, and the failure of equipment is more often than not due to the fact that adverse climatic conditions have not been taken into account. It is all too easy to design for operating in high ambient air temperatures and fail to recognise the importance of high humidity, dust loading, etc.

The complex nature of the odour problem means that all too often equipment installed is ineffective, not because of bad design but because of incorrect application. The days of trial and error are over, the technology is available to solve the problem.

The aim of this Paper is to give the reader an insight into the complex nature of the problem, methods available for treating odours and why a lack of knowledge in what is a highly-specialised field can result in the selection of an inferior system.

#### THE CHEMISTRY OF ODOURS

Septicity is usually associated with the formation of hydrogen sulphide  $(H_2S)$ . However, under such conditions many other malodorous compounds are formed all of which contribute to the overall problem. These include:

| R.SH                                                       |
|------------------------------------------------------------|
| Ar.SH                                                      |
| R.S.R <sup>(1)</sup>                                       |
| R.S.S.R. <sup>(1)</sup>                                    |
| R.S.S.S.R <sup>1)</sup>                                    |
| R.NH <sub>2</sub> ,R <sub>2</sub> :NH<br>R <sub>3</sub> :N |
| R.COOH                                                     |
| R.CHO                                                      |
| R.CO.R <sup>(1)</sup>                                      |
| R.OH                                                       |
|                                                            |

As reported by Harkness<sup>(1)</sup>, the formation of sulphide is probably the commonest and most troublesome mainifestation of septicity in sewerage systems. The reactions are part of the natural cycle of changes which sulphur and its compounds undergo as a result of biological activity. The cycle (Figure 1) involves both oxidation and reduction reactions but since such reactions are an essential feature of all living systems they are not necessarily related to whether the change takes place under aerobic or anaerobic conditions. The formation of free hydrogen sulphide  $(H_2S)$  normally takes place under anaerobic conditions by the bacterial breakdown of organic compounds containing sulphur in a reduced state and from sulphate sulphur  $(SO_4^-)$ . Sulphur occurs in a reduced form in amino acids, eg:

> Cysteine Cystine Methionine and Taurine

As reported by Sikora el  $al_{i}^{(2)}$ , Methyl sulphide  $(CH_{3}.S.CH_{3})_{i}$ methyl mercaptan  $(CH_{3}.SH)_{i}$ , and dimethyl disulphide  $(CH_{3}.S.S.CH_{3})_{i}$ can be derived from methionine, and ethyl sulphides can be formed similarly from appropriate compounds of sulphur.

The latter compounds can, as reported by Matthews et al<sup>(3)</sup>, also be formed from chemical reactions between hydrogen sulphide and certain unsaturated ketones, and such a reaction with mesityl oxide  $(CH_3, COCH=C (CH_3)_2)$ ; has caused "catty" odours from works in the London area.

Volatile fatty acids; alcohols; and ketones; are produced by carbohydrate fermentation, compounds reported (1) are pyruvic acid (CH<sub>3</sub>; COCOOH); formic acid (H.COOH); acetic acid (CH<sub>3</sub>CHOOH); propionic acid (CH<sub>3</sub>CH<sub>2</sub>COOH); butyric acid (CH<sub>3</sub>CH<sub>2</sub>COOH), ethyl alcohol (CH<sub>3</sub>CH<sub>2</sub>OH), butyl alcohol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH); isopropyl alcohol (CH<sub>3</sub>CHOHCH<sub>3</sub>); acetone (CH<sub>3</sub>COCH<sub>2</sub>); and butanediol (CH<sub>3</sub>CHOHCHOHCH<sub>3</sub>).

The Stickland reaction between pairs of amino acids can also yield higher carbon number fatty acids.

Amines are produced from amino acids by decarboxylation, ie. removal of the -COOH group, examples being amino butyric acid (COOH.  $CH_2 CH_2 CH_2 NH_2$ ) and Cadaverine ( $NH_2 (CH_2) = NH_2$ ).

Methylamine  $(CH_3NH_2)$  and dimethylamine  $(CH_3)_2NH$ ) are found in urine and therefore may occur in sewage.

Metabolism of the amino acid tryptophan can produce indole and indole acetic acid with conversion of the latter to skatole which is known for its faecal odour.

Finally, it must be remembered that proteins, amino acids, and fatty material are major constituents of the organic matter of domestic sewage with readily fermentable carbohydrates as lesser constituents, so that all sewage can become malodorous in the absence of oxygen even without the formation of sulphide from sulphates.

It can be seen from the above complex nature of the problem that has to be faced as well as the technical difficulties involved in finding a solution.

## ODOUR THRESHOLD VALUES

All the malodorous compounds can be detected by smell at very low concentrations in air, therefore even very small quantities of malodorous air can produce a highly offensive smell that disperses over a wide area. Table I lists the odour threshold values for the major malodorants associated with sewage-treatment processes.

Although Table I illustrates that odour threshold of individual components, the complex nature of odour mixtures and interactions in the perception of odorants in a mixture means they have little practical use. To this end have been developed methods for quantifying odour problems.

#### QUANTIFYING THE ODOUR PROBLEM

As a result of recommendations made by the working party on the supression of odours(8) a programme of research on odour control was carried out by the U.K Department of the Environment's Warren Spring Laboratory (W.S.L). Part of this programme (9) was to develop improved techniques for both sensory measurement and instrumental analysis of odours.

As reported by Bailey et al (10) the two main parameters measured by the W.S.L. were:

Dilution Factor (d)

This is the number of times a sample of gas has to be diluted with odour-free air before 50% of a panel of observers will just not detect an odour.

Odour Emission (E)

This is the product of the dilution factor and flowrate for that source of malodour.

As d is dimensionless; E has dimensions of volume per unit time; eg,  $m^3/s$ . The techniques developed by W.S.L. were employed to study odours at a sewage-treatment works in the U.K as part of a joint investigation project carried out by W.S.L. for the Water Research Centre (W.R.C.). Results of the Sensory measurements(10) are presented in Table II.

The Table illustrates the importance of not simply relying on odour intensity when evaluating a problem, in respect that although air released from high-rate biological filters is of relatively low intensity in practice they can constitute a serious odour nuisance due to the high flow rates involved, that is Odour Emission (E) is the critical parameter.

It also illustrates how points of turbulence within the process stream can result in odour problems, in particular pumping stations.

In view of the high ambient summer temperatures experienced in the Middle East it would be prudent to assume dilution factors are increased by a factor of at least 2.

Two final conclusions can be drawn from Table II; the futility of over ventilating the source of odour in an attempt to solve the problem in respect that the dilutions achieved are small compared to what is required even for the least offensive of operating and that to the general public even the least-offensive process can give cause for complaint.

There has also been considerable work done on analysis of complex odour mixtures. Bailey(11) recently concluded that very few odour problems are the result of a single malodorous compound, having undertaken collection and analysis using a preconcentration stage followed by gas chromatographic techniques to identify "The complexity and quantify the majority of compounds involved. of odour mixtures, the very wide range of threshold concentrations of individual compounds and the complex interactions in the perception of odorants in a mixture, make the interpretation and utilisation of data from the instrumental analysis of odours an even more difficult task than the analysis itself. Nevertheless, such analysis has considerable use in identifying species in an odour stream, leading perhaps to changes in the process producing the odour and to better choice; design and operation It is hoped that on-line control of of abatement equipment. such equipment will become available in the future. At present on-line control is only possible with one compound or class of compounds, at very low concentrations (eg certain sulphur compounds), from which one then has a reliable indicator of total quantity of odour. One fact that has clearly emerged is that many odours are complex mixtures and are subject to change with changing raw materials or process conditions. This has an important bearing on the choice and design of abatement plant in that off-the-shelf solutions are rarely satisfactory, and a thorough testing and assessment programme leading to a tailor-made design is usually required."

#### CONFINING THE ODOURS

Even very small quantities of malodorous air can produce a highly offensive smell that can disperse over a wide area. The prime objective of any scheme must therefore be to confine and isolate the malodorous air at source. In addition it must be emphasised that almost all the compounds, if simply confined, can reach toxic concentrations and possibly even explosive limits; therefore ventilation is an important factor as isolation. With certain it is necessary only to isolate the individual sources of odour, eg sludge-holding tanks; whereas with others, such as sludge-press houses, sewage-pumping stations, it may be necessary to enclose and maintain the whole premises under negative pressure due to generally offensive air throughout the building. In this respect building design has a considerable bearing on how easily this can be achieved.

Dividing walls within the main building can be used to prevent foul air contaminating clean areas. For example, dry pump sumps are only offensive if foul air is allowed to escape into them from contaminated areas. Therefore although it may be necessary to ventilate dry pump sumps to remove heat liberated from electric motors, providing the air is clean it can be extracted directly to atmosphere without treatment.

In wet areas, where practical, consideration should be given to the use of removable GRP covers to enclose both equipment and open channels. This allows foul air to be confined at source, be extracted with relatively low air-flow rates and considerably improve working conditions for operators. Although installing covers involves additional expense; it can often be justified by the savings made by reducing the air-flow rate to be treated and by savings made in respect of general plant maintenance due to reducing corrosion problems.

In addition there are certain procedures of operating mode that can be applied to reduce the problem. Although malodours are liberated from stagnant effluent; excessive turbulence greatly aggravates the problem. Discharge of effluent from high level into wet wells is a prime example. By discharging through a dip pipe extending to below the water surface; odour levels can be greatly reduced. This also applies to the discharge of pressure mains; where malodorous gases dissolved under pressure in the effluent are released on decompression.

The capital cost of any odour-abatement system; to a large extent; is dependent on the air-flow rate involved. Extraction rates should therefore be kept to the minimum sufficient to not only prevent leakage of odours but also to prevent potentially dangerous conditions occurring; while at the same time maintaining acceptable working conditions for operators. To design an extract system solely on the number of air changes per hour is not good practice; for while it may satisfy the last two criteria it cannot be guaranteed to confine the odours within the structure.

#### EFFECT OF WIND ON A STRUCTURE

The rate of ventilation required for the effective containment of airborne contaminants released within a building depends mainly on the airtightness of the structure. In a perfectly sealed enclosure ventilation would only be required to dilute and remove contaminated air. However, no buildings are completely airtight. Imperfections in the structure and such openings as windows and doors allow air to pass to and from the building. The larger the gaps in the structure are the greater the rate of air through the building and, as a consequence, the greater will be the rate of extract ventilation required to contain any contamination. Thus there are significant advantages in first ensuring that the building is as well sealed as practicable. The natural forces which give rise to this movement of air through a building are the result of wind and temperature effects. Wind causes air to enter through gaps and openings on the windward side of a building and leave through similar apertures on the leeward side. A temperature higher inside a building than outside similarly causes a movement of air but<sub>2</sub> in this case; it enters at low level and leaves at high level. The reverse pattern of movement occurs when the indoor temperature is lower than that outdoors. The effects of wind are generally more predominant. It is advisable, therefore, to build a windbreak (eg another building) upwind of the buildnig in which odour is produced, where this is possible.

The infiltration area is basically defined as the sum of the sum of the areas of the gaps and openings (leakage areas) in the least airtight external wall which may face directly into the wind. Walls which are completely sheltered by adjacent structures need not be considered.

For a square or nearly square building (up to an aspect ratio of 1.5) the possible effect of wind impinging on two sides at the same time should be considered.

Wind speed increases with height above ground and the degree and extent of the variation depends on the "roughness" of the landscape over which the wind is passing. Over open country the effect applies up to a height of 280m and over wooded countryside it applies up to 400m. The meteorological wind speeds are related to a standard height of 10m on open and unobstructed sites. Thus it is necessary to determine the corresponding wind speed for the area involved at the building height, which in turn allows the pressure difference being generated by the wind across the building to be calculated.

When air is being mechanically extracted from within the building to prevent exfiltration; this pressure difference will act across the windward wall.

The rate of infiltration may then be derived from the pressure difference and total infiltration area. Typically this could vary from  $2-20 \text{ m}^3 \text{ air/s/m}^2$  of infiltration area.

In assessing the leakage areas of walls (and roofs); all gaps and openings where air leakage can occur should be taken into account. Joints and overlaps in cladding may provide air leakage paths particularly at the wall/roof boundary. For large apertures; such as doors, the leakage area should be taken as the maximum openable area. For openable windows and doors which normally remain closed the leakage area should be measured.

This shows the advisability of having non-opening windows and to seal up existing openable windows; also how failure to close a personnel-access door results in an immediate leakage area of  $2m^2$ . Good housekeeping and operator awareness of the consequences of not closing a door are essential if the problems are to be overcome.

Some buildings have rooms along one or more sides so that air, before passing into the central area of the building has to flow through two walls in succession. In such instances, it is necessary to take into account these internal walls when calculating the infiltration area. Internal walls therefore can help considerably to reduce the leakage area.

With all this data available; the expert can advise on what type or types of system are required to provide an economical solution.

Correct ventilation-system design is essential to ensure efficient movement of air and odour removal.

Extracting air from relatively clean areas through foul areas allows the designer to utilise the air extracted to a maximum, by achieving a greater number of air changes within a particular area while not increasing the overall extract rate. All the malodorous compounds are denser than air; for example; hydrogen sulphide has a vapour density of 1.189 compared to air as 1.00; and such compounds tend; therefore; to concentrate at low level. Careful thought must be given to positioning the extract ducting in order to prevent potentially dangerous levels of these toxic compounds occurring.

#### METHODS OF ABATEMENT

It is not practical within the scope of this paper to detail the criteria for all methods of abatement available, nor would it be wise to attempt to condense such information as this could be misleading.

There is a wide range of equipment available for treating malodorous air; none however is suitable for treating every odour problem and therefore great care is needed in selecting the system to be installed. Lack of knowledge in what is a highly-specialised field can result in the offender selecting an inferior system. It is essential to investigate all the possibilities and to seek expert advice as it is all too easy to be misled.

Criteria such as air-flow rate; temperature; humidity; malodorous compounds involved, odour strength; topography; climatic conditions etc.; all have to be taken into account in determining the efficiency required to abate the nuisance.

Below are listed the major methods of abatement employed, along with their general advantages and disadvantages.

Stack Dispersion is often used as a means of reducing odours, the object being to release the malodorous air at a sufficient height above ground level so that after mixing with the atmosphere they are diluted such that by the time the odours again reach ground level they have been diluted to below their threshold of smell. Where highly-odorous air streams are involved it is usually impractical to install a stack of sufficient height to ensure odour abatement. Even with correct design there is always the possibility, when the wind is gusting, that downwash conditions arise where gusts of virtually undiluted odour can be detected, in the vicinity of the base of the stack which then disperse over a wide area.

Although unsuitable for highly-malodorous air streams, stack dispersion can play an important part by dispersing residual odours emitted from the primary treatment system.

<u>Masking Agents</u> are organic compounds that are injected into the malodorous air stream to counteract the unpleasant smell. A wide variety of different agents are available for specific odour problems. Masking Agents are commonly employed because of ease of installation, flexibility, and versatility in use. Care has to be taken in selecting the agent as certain combinations of odour/masking agent can produce an equally offensive smell. Dilution of the masking agent to below its threshold of smell can occur before the malodour has dispersed and although the desired effect is achieved near the source the problem can be still apparent a distance away. Different rates of diffusion of malodour and masking agent can produce a similar effect.

Ozone-Gas-Phase Oxidation has been widely used both in America and the U.K. Although ozone is one of the most powerful oxidants known; recent work into gas-rate reaction constants as reported by Warren Spring Laboratory<sup>(8)</sup> show that considerable reaction times are required to ensure complete reaction. Each compound reacts at a different rate; the majority far slower than hydrogen sulphide; in addition reaction rates are dependent on temperature; the cooler the mixture the longer the reaction time required. Care is also required in controlling ozone dosage to ensure that under conditions of fluctuating odour levels a high and dangerous residual of unreacted ozone is not discharged to atmosphere. In general it is impractical to build holding chambers with retention times greater than 30 seconds and only compounds that react rapidly are likely to be significantly destroyed in that time.

Thermal and Catalytic Oxidation All malodorous compounds are capable of being combusted to their end oxidation products of  $CO_2$ ;  $H_2O_7$ ,  $NO_7$ ,  $NO_2$ ;  $SO_3$ . Although incinerators can give a high efficiency of odour removal; the expense involved in raising moist ambient air to sufficient temperatures for the oxidation to proceed severly limits their use. In general temperatures of 650°C-800°C plus are required for thermal incineration, while catalytic incinerators can achieve the same result at reduced temperatures, 250°C-450°C being typical. Although running costs can be further reduced by use of heat recovery; usually in the form of pre-heat to the incoming foul air, the use of incinerators is usually restricted to problems where contaminants are in concentrations such that on combustion their calorific value makes a practical contribution in reducing Care has also to be used when using catalysts; running costs. particularly precious-metal ones as halogens and sulphur oxides, if in sufficient concentrations, can inhibit catalyst efficiency. The presence of heavy metals in the exhaust can also lead to poisoning and deactivation of the catalyst.

<u>Absorption Systems</u> using activated charcoal are commonly used for odour treatment and a wide range of different carbons are available. The nature of the starting material, method of carbonisation and activation has a marked influence on the properties of the final product and careful selection of the adsorbent is required to ensure maximum efficiency and operating life. Process gases containing solids, water droplets or very high humidity are often unsuitable for treatment by adsorption without some form of pretreatment, eg filtration, or preheating the foul air to reduce R.H. (relative humidity).

In addition to carbon-based adsorbents there are also available ones based on alumina impregnated with a reactant, eg potassium permanganate to oxidise the malodorous compounds adsorbed. As the reactant is itself reduced in turn bed life is limited.

It has been reported (12) that the addition of a few ppm of ozone to the foul air prior to the carbon adsorber can considerably increase bed life; presumably by oxidation of the malodorous compounds by the ozone which is itself absorbed.

Absorption Systems remove gaseous odours from the air by absorbing it in a liquid. Although, in principal, one should be able to absorb any odorant with water, due to the low solubility of most groups of malodorous compounds it is impractical to achieve a sufficient degree of removal using water alone. Occasionally it is practical to use, for example, sea water on a once-through basis as a pre-absorption state to reduce extremely-high odour levels. However, almost all absorbers are expected to operate with liquid being recirculated to minimise operating costs. This can be achieved by using in the liquid a reagent that reacts with the odorant, even so a small proportion of liquid (usually 5%) is bled-off to allow make-up with fresh reagent.

Although a reagent can be selected for a specific malodorous compound very few odour problems are the result of a single compound and again great care is required in selecting reactants of which a great many are available.

Neutralising compounds, eg, acids and alkalis, have the disadvantage that reactions are reversible so odorants can be desorbed from liquid effluent. They are also specific and while alkaline reagents will remove fatty acids, sulphides and mercaptans, acidic reagents are required to remove amines. For these reasons, as odorous air generally contains both basic and acidic compounds, along with compounds that react with neither alkaline nor acid, they are often used in conjunction with an oxidising agent.

Hypochlorite; the most common oxidant used; again is pH-dependent. For example; at below pH2 it forms chlorine water; between pH2-6 hypochlorous acid and above pH6 hypochlorite. Again some malodorants will be removed more effectively in alkaline solution; while for others the efficiency may be greater in acid solution. As reported by Carleton(13) chlorination reactions can result in reaction products being more odorous than the original odorants and also more toxic; eg, chlorophenols and chloramines. Chlorine dioxide which is also used is less likely to produce chlorinated compounds but tends to desorb, producing a strong odour which could only partially be removed in a secondstage sodium hydroxide absorber.

When treating a complex odour problem with hypochlorite, such as those associated with sewage treatment, it is not uncommon to have to incorporate two-or even three-stage absorption, each operating under different pH conditions. Care has to be taken with bleed-off liquors to prevent inter-reaction and a possible secondary odour problem.

The use of ozone for water treatment is well established. Its use as a reactant in absorption systems is relatively new; but one that is increasing in popularity. The disinfection properties of ozone are well documented as is its ability to provide disinfection equal to chlorine-based oxidants but with considerably lower dose rates and reaction times; it is less susceptible to changes in water temperature and pH and produces no harmful by-products and these properties its potential as a reactant. Ozone is a sparingly-soluble gas and hence specialised techniques are required to achieve a high degree of dissolution. The addition reactions of ozone with unsaturated double-bond compounds are common knowledge; the fact that ozone will oxidise all the major groups of malodorous compounds listed previously is not. It is capable of operating under neutral, alkaline or acid pH; although at high pH the rate of decomposition is increased. As with other reactants the mode of operation is determined by the problem and as others can be used in twoor three-stage systems. In general, for the correction of sewage-treatment odours, a single-stage system only, without pH control, is all that is required and at the same time achieves a high "kill rate" of airborne bacteria (14). The use of ozone in the aqueous phase overcomes the problems associated with gas/gas contact systems.

#### THE "WET OXIDATION PROCESS"

The potential for using ozone as the oxidant in absorption systems has been discussed briefly above.

The author's company; Ozotech; through its involvement in ozone technology has developed and refined these basic principles of using ozone to produce a well-proven and highly-efficient system for treating sewage odours, the "Wet Oxidation Process".

In the general introduction on absorption systems it has been shown that, in principle, it should be possible to absorb any malodorous compounds simply, with water. Unfortunately the majority of the compounds involved and the worst offenders in particular, the sulphur compounds, are relatively insoluble (for example the Henry's Law constant in water for  $H_2S$  is 483 atm/mole fraction). Therefore, irrespective of the contact time in the absorber or the liquid-to-gas ratio applied, it is not possible to achieve the removal efficiency required to solve the problem.

To illustrate the point Carleton<sup>(13)</sup> reports that to remove 99% of a fairly insoluble odorant, propyl mercaptan (Henry's Law constant in water 350 atm/mole fraction) from an air stream flowing at  $5m^3/s$  in a reasonably-sized absorber (200m<sup>3</sup> of packing) it would be necessary to use 20,000 m<sup>3</sup>/h of water, on a oncethrough basis.

By using a reactant, absorbers are able to operate with liquid recirculation and although it is necessary to bleed-off a small proportion of liquid to drain to allow more reactant to be introduced and to prevent the liquor becoming saturated with reaction products, absorption can be made a viable process.

The general principle of a countercurrent packed absorber with liquid recirculation is illustrated in Figure 2.

By using his experience in selecting the optimum design parameters the expert can design the absorber to suit the specific requirements of the particular problem.

The variables open to him are:

- (a) Choice of reactant and dose rate.
- (b) Choice of tower packing.
- (c) Volume and height of packed bed.
- (d) Tower gas velocity
- (e) Liquid-to-gas ratio, L/G.
- (f) Recirculation ratio; L/D.

The above list illustrates the endless number of permutations open to the designer and reaffirms why it should be left to the expert.

## OZONE AS THE REACTANT

There are several criteria the reactant must meet to be of use in the absorption process for odour applications.

It must be soluble in water and, although ozone is only a sparingly-soluble gas, the use of specialised techniques enable this to be achieved.

It must be capable of reacting rapidly with all the compounds involved (contact time 3 seconds maximum) to produce soluble reaction products.

As the liquor is recirculated reaction must be completed in the 1-2 minute dwell time in the sump; and the reaction products must not be malodorous.

Reaction products and residual reactant in the bleed-off liquor must not create an effluent problem.

Ozone meets all these requirements and destroys the malodorous compounds by oxidising them to soluble non-odourous ones; in certain cases to their end oxidation products of  $CO_2$  and  $H_2O$ . Major reaction equations are shown in Table III.

#### OZONE PRODUCTION

Ozone is produced by the action of a silent high-voltage electrical discharge on extremely dry air; the majority of the power input being liberated as heat that has to be removed. There are therefore two main criteria that have to be met to ensure reliable trouble-free operation of ozone generators: first; air with a very low dewpoint and, second, efficient cooling of the ozone production elements.

There are two types of absorption dryers used with ozone generators. These either operate at atmospheric pressure or under pressure and, in general, the mode of operation of the ozone generator will be determined by the drying method applied.

Irrespective of which type of dryer is used it is necessary reliably and continuously to achieve air with a dewpoint of better than -50°C. This is achieved by installing twin drying cells so that while one cell is operating drying the air, the second cell is being regenerated ready for the next cycle. On pressure dryers this is achieved by using a portion of the dry air from the cell in operation to regenerate the spent cell by atmospheric decompression.

Atmospheric air drying is more difficult and requires far larger drying beds to achieve the same result. They are also regenerated by passing heated air (200°C) countercurrent through the bed. In addition, adsorption of moisture is an exothermic process (ie heat is released). Although this does not create a problem on pressure dryers where the adsorption cycles are short, on atmospheric dryers the increase in bed temperature can create serious problems since the higher the bed temperature the lower the dewpoint that can be achieved (for this reason it is not uncommon to install cooling coils within the absorption bed).

As mentioned previously, the majority of the power input used to generate ozone is liberated as heat, irrespective of ozoniser type or manufacturer. Therefore efficient cooling is essential to prevent damage to the ozone production elements.

It is always more difficult to achieve the same heat exchange/ transfer using an air to air system than with an air to water one, particularly when the air available has a high ambient temperature. This very much favours the use of water-cooled ozone generators as opposed to equipment that is air cooled.

Ozotech Ltd. can supply both atmospheric-and pressure-operating water-cooled ozonisers for use with the "Wet Oxidation Process"; the final selection being determined by such factors as production capacity; ozone dose rate required and climatic conditions under which the system has to operate. These factors are particularly relevant when installing equipment in hot climates; as; for example, experienced in the Middle East.

Ambient air temperatures of  $45^{\circ}$ C dry bulb;  $31^{\circ}$ C wet bulb; as experienced in the Middle East may not, at first sight, appear to be a problem. However, these conditions correspond to a moisture content of  $23gH_2O/kg$  dry air. When this is compared to typical European conditions of  $20^{\circ}$ C; 80% R.H. and  $12gh_2O/kg$ dry air it is apparent that almost twice as much water has to be removed from the ambient air entering the ozoniser.

The problem is further aggravated by the fact that in such climates far higher odour concentrations are experienced; these require far higher ozone dose rates and hence production capacity for a given volume of foul air as compared to European conditions.

Damp air is by far the greatest single cause of problems when operating ozone generators under hot climatic conditions.

If atmospheric ozonisers are selected then the packaged generator/ driers must be located in an air-conditioned room where the available air is at a dewpoint not exceeding 18°C.

If pressure ozonisers are selected with pressure-operated air driers then the following additional equipment is recommended. A cooler after air compression to cool the air back to near ambient temperature and a pre-cooler (fed by chilled water) prior to the drier to condense out further water in the compressed air thus greatly reducing the load on the air drier.

Water for cooling the ozoniser is usually in limited supply and often has too high a temperature. For efficient operation of ozone generation, under hot climatic conditions, water cooling (as opposed to air cooling) is essential and it is recommended that a chilled-water system operating on a recirculating loop is used. (See Figure 3).

## APPLICATION

Figure 4 shows the basic principles of the "Wet Oxidation Process". Ozonised air from the ozoniser (19) is drawn into the scrubbing water by means of a hydraulic injector (9) using the head from the wash-water pump (8). Patented "Helimixers" complete the emulsification of the ozonised air/water (7).

Trace amounts of ozone not dissolved in the water are mixed with the foul air (1) extracted from source by a fan (2) and deodorised in the scrubbing tower (3) by the action of tower packing and wash-water sprays (4). The treated air passes through a mist eliminator (5) where entrained water droplets are removed prior to discharge through a stack (6) to atmosphere. To prevent saturation of the water with oxidation products, make-up water is added to the sump (12), with an overflow to drain (11).

As ozone controller can be used to provide automatic control of ozone production to demand.

# ANALYTICAL RESULTS

Figure 5 shows a typical ultra-violet spectrograph of air from a sewage plant being treated using the "Wet Oxidation Process"; measured over a full spectrum ranging from 200mm-300mm wavelength. Over 40 peaks have been identified and a comparison can be made; in terms of the reliable height of each peak before and after treatment (18).

Trace A is of the untreated foul air; trace B shows the intermediate stage after preozonation (ie after mixing with the undissolved ozone gas); and trace C the treated air leaving the scrubbing tower. Peaks 1 to 13 are mainly amines; and ammonia compounds. Peaks 14 to 25 are mostly oxides; elemental oxygen and ozone; and Peaks 26 to 27 sulphur compounds.

It can be clearly seen by comparing traces A and B that the effect of ozone is to reduce both the amines and sulphur compounds, and further reduce them after scrubbing as shown by trace C. To appreciate the full effect it is necessary to note the changing points of scale magnification.

# MICROBIOLOGICAL CONTAMINATION OF THE AIR

In addition to the odour problem there is undisputed evidence that air exhausted from enclosed sewage-treatment works cause pollution by micro-biological contamination of the environment.

As the majority of sewage pumping stations are located within densely-populated residential areas serious consideration should be given to controlling this pollution.

Dr. H. U. Wanner <sup>(14)</sup> of the Occupational Hygiene Institute at the Eidgenossiche Technische Hochschule in Zurich, who is well known for his work on the microbiological content of air at open sewage-treatment works; has studied this problem. He concludes from the bacteriological results; that the risk of airborne infection for persons at an enclosed plant is greater than at an open plant because airborne bacteria counts are considerably higher than those registered at open plants. On the other hand; analyses of air from a properly-ventilated enclosed plant after treatment by the "Wet Oxidation Process" show clearly that bacteria counts are of the same order or less than normal atmospheric levels.

The results of Dr. Wanner's findings are shown in Table IV.

Samples were taken on 12.12.1973 using a split-spanner nutrient medium; BA = blood agar and PC = plate count agar (total bacteria count). The conclusion of this reported work is that the ozone wet oxidation process is able to remove a large proportion (about 90%) of the micro-biological contamination collected through ventilation systems in enclosed plants and so performs an additional benefit to that of odour treatment.

### DESIGN PARAMETERS

It has been shown previously that there are many options open to the engineer when designing an absorber. There are, however, when designing a "Wet Oxidation System" certain defined routes to follow step by step to arrive at the final solution.

The air-flow rate to be treated is obviously the most important; not only in respect of containing the odours but also in its relationships to odour levels in the air; so allowing the odouremission rate to be determined. From the emission rate the ozone dose; and therefore the hourly production rate; air compressor and cooling systems requirements; can be determined. The ozonised air-flow rate determines the water requirements for the hydraulic injector/contacting system necessary to achieve the desired dissolved ozone concentration.

The air-flow rate for treatment; odour level; and ozone dose rate all have a bearing when deciding on the wash-water recirculating rate; which combined with the injector-water-flow rate/pressure-drop requirements allows the wash-water-pump duty to be specified.

Only at this stage is it possible to start designing the actual absorber. From the liquid-to-gas ratio (L/G) the type, size, and volume of tower packing can be chosen to produce maximum correction efficiency while maintaining an acceptable pressure drop across the absorber.

The bleed-off and make-up water rate to the tower is based on a combination of evaporation losses and rate of production of oxidation products. Fan head is governed by head loss across the absorber plus the extract-ducting pressure levels.

### RUNNING COSTS

Operating costs vary with ozone demand; fan head; etc.; the figures quoted in Table V are typical for a system operating under Middle East climatic conditions; treating 10,000m<sup>3</sup>/h foul air.

#### MATERIALS OF CONSTRUCTION

Ozone is not only a powerful oxidising agent but, also is extremely corrosive particularly in the aqueous phase; therefore, selection of suitable materials is of prime importance. To aggravate the problem climatic conditions experienced in the Middle East in respect of ultra-violet levels severely limit the use of certain plastics.

When designing a system for operation in such conditions it is necessary to use the best materials; eg; high-grade stainless steels; uPVC wrapped by GRP; PTFE; and Hypalon.

#### CONCLUSIONS

The above has shown that it is not possible to generalise about either the problem or the solution. All too often equipment is faulted, not because of incorrect design, but because of incorrect application.

Considerable savings can be made by adopting a less professional approach to the problem, both technically and equipment wise. Although this could reduce capital cost, in the long term it would be a false economy. Every possibility should be investigated and although capital investment and running expenditure are important, care should be taken not to allow cost to be the main aspect which influences the final decision if complete odour removal is to be achieved.

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# TABLE I

# Odour threshold values

| Compound            | Odour threshold<br>ppm by volume | Ref. |
|---------------------|----------------------------------|------|
| Hydrogen Sulphide   | 0.00047                          | 4    |
| Dimethyl Sulphide   | 0.001                            | 4    |
| Dimethyl Disulphide | 0.0076                           | 5    |
| Diethyl Sulphide    | 0.068                            | 7    |
| Methyl Mercaptan    | 0.0021                           | 4    |
| Ethyl Mercaptan     | 0.001                            | 4    |
| Methylamine         | 0.021                            | 4    |
| Dimethylamine       | 0.047                            | 4    |
| Trimethylamine      | 0.00021                          | 4    |
| Ethylamine          | 0.27                             | 6    |
| Diethylamine        | 0.02                             | 6    |
| Skatole             | 0.22                             | 7    |
| Mesityl Oxide       | 0.017                            | 6    |
| Acetic Acid         | 1.0                              | 4    |
| Propionic Acid      | 0.028                            | 6    |
| Butyric Acid        | 0.001                            | 4    |
| Ethyl Alcohol       | 0.1                              | 6    |
| Butyl Alcohol       | 0.12                             | 6    |
|                     |                                  |      |

# TABLE II

| Unit Operation                                                    | Range of<br>dilution factor |
|-------------------------------------------------------------------|-----------------------------|
| Inlet screens                                                     | 250 to 1300                 |
| Detritor                                                          | 180 to 210                  |
| Inlet channel                                                     | 500 to 1300                 |
| Balancing tanks (agitated surface)                                | 3000 to 3700                |
| Primary sedimentation tank<br>(no sludge pumping)                 | 360 to 550                  |
| High-rate biological filter                                       | 500 to 2600                 |
| Biological filters                                                | 150 to 900                  |
| Aeration tank - inlet                                             | 1500 to 400                 |
| Aeration tank - outlet                                            | 170 to 400                  |
| Clarifier                                                         | 1000                        |
| Humus tank                                                        | 500                         |
| Settling tank                                                     | 450                         |
| Pump well of primary sedimentation tank;<br>during sludge pumping | 300000 to 400000            |
| Digested-sludge tank                                              | 4500                        |
| Digester gas (from gas main)                                      | 1600000                     |

Dilution factors for samples taken at a sewage-treatment works in the months of November and August



Major reaction equations for ozone

# TABLE IV

Air-bacteria counts inside and outside plant rooms of the treatment works at Le Pierrier; Montreux; Switzerland

| Pla<br>Mea | ce of<br>surement                 | Nutrient<br>medium | Bateria/m <sup>3</sup>                   | Average            |
|------------|-----------------------------------|--------------------|------------------------------------------|--------------------|
| 1.         | Plant Room<br>(middle)            | BA<br>PC           | 3300,3300,2700,330<br>4600,4500,4400,370 | 0 3,150<br>0 4,300 |
| 2.         | Air outlet<br>(Stack)             | BA<br>PC           | 47; 120; 73; 10<br>366; 207; 360; 32     | 7 87<br>6 315      |
| 3.         | Air outlet<br>(equipment<br>room) | BA<br>PC           | 167, 247, 200, 18<br>347, 334, 300, 33   | 7 200<br>6 342     |
| 4.         | Lakeside                          | BA<br>PC           | 292, 232, 238, 16<br>428, 560, 446, 26   | 7 232<br>9 451     |

TABLE V

| Equipment       | Power Consumption<br>Wh/m <sup>3</sup> air being treated |
|-----------------|----------------------------------------------------------|
| Air compressor  | 0.15                                                     |
| Ozone generator | 0.35                                                     |
| Water chiller   | 0.25                                                     |
| Washwater pump  | 0.45                                                     |
| Extract Fan     | 0.46                                                     |
| TOTAL           | 1.65 Wh/m <sup>3</sup> air                               |





#### SYMBOLS

- D Molar flowrate of make-up or bleedoff liquid.
- G Molar flowrate of gas.
- L Molar flowrate of liquid through absorber.
- H Height of packed bed.
- VG Gas velocity up the tower.

Figure 3

The production of ozone in hot climates: the importance of air pretreatment for small-scale ozone generators



- 6.07 m<sup>3</sup>/h of air at 45°C D.B.; 31°C W.B. equivalent to 6.5 kg dry air/h contains 146.9 g water; and has a heat content (enthalpy) of 187.5 W.
- 2. Compressing the air to 7 bar gresults in increase in air temperature of typically 40°C to 85°C. Although the actual volume of air is greatly reduced and hence water solubility pro rata at 85°C the saturation humidity is greater than the water content. Therefore, no water condenses. The enthalpy of the air has increased to 263.3W.
- 3. An air-blast cooler fitted to the compressor cools the air to within 5°C of ambient, ie 50°C. At this temperature the saturation humidity has decreased from 75  $gH_2O/kg$  dry air at 85°C to only 11  $gh_2O/kg$  dry air. This results in 75.4 g water being condensed and removed, ie 51.3% of the total water is removed. The enthalpy of the air decreases to 142.6 W.
- 4. A water-cooled heat-exchanger (using water previously used to cool the ozoniser) cools the air further; typically to 28°C. At this temperature a further 52g water condenses; ie the initial water content of the air has now been reduced by 86.7%. The enthalpy of the air is now 64.4 W.
- 5. By using air pretreatment the dryers are now able to achieve the desired dewpoint of -50°C. At this dewpoint the moisture remaining is only 0.156 g; ie a total of 99,9% has been removed. Of the 6.5 kg/h dry air produced 25% or 1.3 kg/h is used to regenerate the spent cell by atmospheric decompression.
- 6. 5.2 kg/h of dry air is reduced in pressure to 1 bar g maximum and fed to the ozone generator. Ozone is produced by the action of a silent high-voltage electrical discharge. Of the 1.32 kW of power used, only 5% is utilised to produce the 75 g ozone/h. The remainder of the electrical power is released as heat that must be efficiently removed. This is achieved using cooling water from a recirculating water chiller feeding the ozoniser at 15°C and typically returning from the air-pretreatment heat-exchanger at 18.5°C.





Figure 5 Typical UV spectrograph of air from sewage works treated by ozone

