# An Investigation into the Options to Control Hydrogen Sulphide in Industrial Wastewater Treatment Systems.

By: Michael M$^{c}$Grath.

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**Project Supervisor: Dr. John Bartlett**

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## Graphs, Tables, Figures and Plates

# Abstract

A research study examined the options for controlling hydrogen sulphide in industrial waste water treatment systems

It was found from the study that the principal methods of controlling hydrogen sulphide in waste water treatment systems are physical, chemical, biological, or thermal systems.

The physical methods include containment, dilution, combustion, adsorption, activated carbon, sand, soil, compost beds, oxygen injection, masking agents and wet scrubbers.

The chemical methods include chemical oxidation, catalytic filtration, chemical adsorption, catalytic combustion, electrochemical treatment, nitrate dosing, and chemical scrubbing.

Biological methods include trickling filters, aeration tanks, stripping towers, sulphur oxidising bacteria, anaerobic biological reduction and lagoons.

Thermal methods are thermal conditioning, incineration and flares.

The research included:

- A review of available information on sulphide removal and treatment.
- A review of all methods for sulphide removal to determine effectiveness, applicability and removal efficiency.
- A review current of experiences in Ireland with sulphide abatement including three site visits.
- Selection of a method for trial at Aughinish Alumina to abatement sulphide emissions from an industrial effluent treatment process.
- Review of trial results with a view to installation of permanent system.

The trial consisted of the installation of a Bio-reactor which cultured bacteria specific to the treatment of sulphide in wastewaters with low organic content and resistant to pH variations. The bacteria were cultured every day and dosed into the treatment process over a one hour period each day for seven weeks. The result was a sulphide reduction of 97%. The bacterial addition was stopped, and within a two week period, the sulphide returned to its original concentration.

## Acknowledgements

I would like to thank my wife Ita, my children Jack, Kevin, and Hilary for their support and tolerating my absence for many hours throughout the whole MSc programme. Also I would like to thank Aughinish Alumina management for sponsoring me and giving me the encouragement to take up these studies.

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# Chapter 1

## 1.1 Introduction

The purpose of this dissertation is to investigate the state of the art methods of removing Hydrogen Sulphide from waste water treatment systems and to trial a bacterial addition to the clarifier in the waste effluent plant in Aughinish Alumina.

Aughinish Alumina is fully owned by a Swiss company Glencore who are a leading privately held diversified natural resource group. It has world wide interests in mining, smelting, and refining. Its principal business is trading in metals and minerals, energy, and agricultural products.

Alumina is the raw material used by aluminium smelters in the manufacture of the metal aluminium. Alumina itself is refined from bauxite and it takes 2 tonnes of bauxite to produce one tonne of alumina. The world wide production of alumina was about 55 million tonnes in 2002 and Aughinish Alumina produced over 1.5 million tonnes

An alumina refinery is designed to extract alumina from bauxite using a refining process called the Bayer chemical process. This process has changed little in over 100 years and involves dissolving the ground bauxite in a caustic solution at a high temperature and high pressure and carrying out the following unit operation

- Decantation
- Filtration
- Precipitation
- Calcination.

The waste effluent plant in Aughinish Alumina processes all waste water in the plant along with the run-off from the residue mud stacking area. This run-off is dependent on the amount of rainfall as the mud stacking area is over 120 hectares in size. All treated water is discharged to the river Shannon under licence. Discharge to the river can vary in flow between 6,000m$^3$/day and 21,600m$^3$/day, depending on the amount of rainfall.

**Plate 1.1** The 35 metre Clarifier at Aughinish Alumina.

The waste water effluent system comprises two operational stages: neutralisation and clarification. The neutralisation is done by the addition of sulphuric acid and this results in the precipitation of fine gelatinous aluminium hydroxide particles. The particles are removed by the additional of polyelectrolyte to aid sedimentation in the clarifier. The salts generated by the neutralisation of the caustic effluents from around the site are reduced by Sulphate Reducing Bacteria (SRB) to sulphide. This leads to operational, environmental and safety problems.

## 1.2 Aims and Objectives

The Industrial effluent treatment plant at Aughinish Alumina in the past number of years has been unable to cope with the large odour problem caused by the production of hydrogen sulphide. This sulphide is generated by the reduction of sulphate salts generated in the neutralisation of caustic effluent from around the site. The production of the Hydrogen Sulphide causes problems with odours and poor retention of solids in the clarifiers including,

- Production of odorous hydrogen sulphide which can give rise to complaints.
- Operational difficulties with the clarifiers as the hydrogen sulphide gas produced interferes with the blanket formation in the clarifiers
- The poor blanket formation leads to increased flocculant addition to control solids retention.
- Poor solids concentration reduces the filtration effect of the blanket.
- Corrosion levels are increased.
- Hydrogen sulphide is a toxic gas affecting personnel safety.

The aim of this investigation was to find out the present state of the art for methods of removing hydrogen sulphide from water systems and to trial the use of a bio reactor on site to avoid the production of hydrogen sulphide in our effluent plant.

Objectives

- To examine all the options available to control hydrogen sulphide
- Examine odour and general background to odour.
- Examine how hydrogen sulphide is produced.
- Look at case studies.
- Visit other plants and industries that have similar problems.
- Examine all technical options.
- Look at technical options that could be used to solve the Aughinish problem, and
- Undertake trial in A.A.L.

## 1.3 Methodology

Information was gathered from the following

- Science Direct
- University of Limerick Library
- I.T. Sligo Library
- ENFO
- U.S. Patent
- US E.P.A.
- Irish E.P.A.
- E.E.A.
- Barbour Index.
- Site visits
- Discussions with water treatment specialists.
- The Alumina Industry.

Two case studies were examined, three site visits to industries were undertaken, and a trial was carried out to determine the effectiveness of one option for hydrogen sulphide control.

# CHAPTER 2 LITERATURE REVIEW

## 2.1 Odour – General Background

This section introduces the concept of odour and contains information on the following:

- Definition of odour.
- Odour nuisance.
- Odour complaint numbers.
- Odour and health.
- How we perceive odours.
- Attributes of odour.
- Regulatory requirements.
- Odour limits and conditions.

### 2.1.1 What are odours?

In the simplest form, an odour comprises a single chemical species that causes a physiological response in a human. This physiological response can vary from person to person as reported by Van Harreveld *et al.* (1999). Odour emissions comprising single odorants are not widespread and are probably limited to a few pharmaceutical or fine chemical process emissions. In these cases, it is possible to express the odour in terms of concentrations (ppb, $mg/m^3$ etc.). However, an odour usually comprises a number of chemical species that can each cause a different physiological response in a receptor (EPA, 2001).

### 2.1.2 Odour nuisance

The importance of odours at low concentrations in human terms is related primarily to the psychological stress they produce rather than the harm they do in the body. Offensive odours can cause poor appetite for food, lowered water consumption, impaired respiration, nausea and vomiting and mental disorders (Miedema *et al.* (2000). In extreme situations, offensive odours can lead to the deterioration of personal and community pride, interfere with human relations, discourage capital investment, lower socio-economic status and deter growth. (Metcalf and Eddy, 1991).

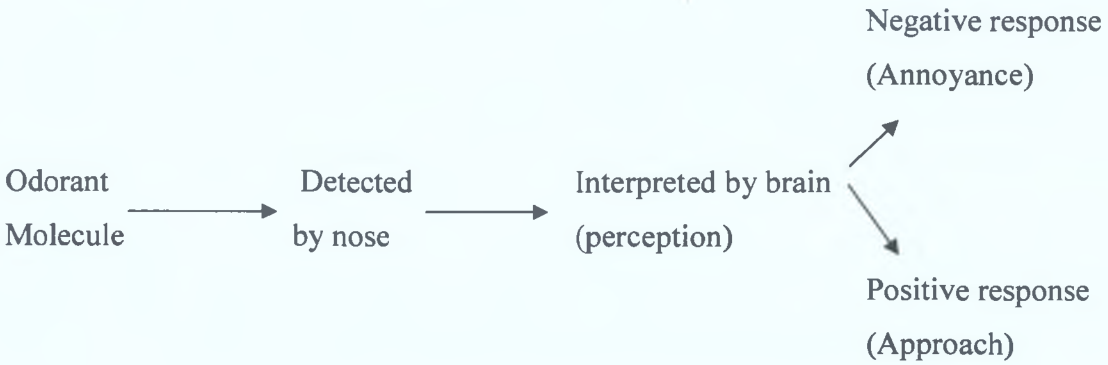
### **2.1.3** Exposure - Dose response.

There are a broad range of human perceptions and responses to a variety of fragrances, aromas, neutral odours and malodours. The range depends on physiological factors, custom, habit and attitude. The concentration with which an odour becomes a nuisance depends not only on its characteristic smell but also on factors which can influence the nose, such as social, regional factors ,air temperaturea and humidity.

.Anzion *et al.* (1994) found that there is no fixed relationship between pollutant concentration and response. Hence, people experiencing the same level of odour nuisance do not necessarily react in the same way.

### **2.1.4** How smells are percieved - physiological principles

The human olfactory sense organs (i.e the nose), along with those for taste, are generally considered to be the oldest in evolutionary development. The stimulation of the human nose produces a signal which induces avoidance or approach behaviour, i.e. if a source smells unpleasant the natural reaction is to move away, but if it is pleasant the tendency is to go towards it (CEN, 1999). The olfactory process and the behavioural responses take place at different levels in the brain and can be represented by the following:



There is however a substantial grey area when it comes to human response to positive and negative odours because odour perception varies from human to human. Some humans will perceive a certain type of smell to be unpleasant whereas others will perceive it to be pleasant. Other examples of how odour perception can vary from human to human are listed below:

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- A strong persistent positive odour can quickly become annoying inducing a negative response.
- After prolonged exposure humans can become de-sensitised to certain odours, e.g. workers at oil refineries often become de-sensitised to the smell of hydrogen sulphide.
- Once a negative response is associated with a particular process, it is often difficult to change the appreciation of the particular odour stimulus in an individual. This is one of the reasons why process operators, after significantly reducing their odour emissions, still receive odour complaints, i.e. even though the odour emitted by the process is less intense, local residents are still able to smell it (they are sensitised to that smell) and hence, they continue to lodge complaints.

The following example describes a specific example of the problems associated with odour perception: A large vegetable processing facility was located on the edge of a large town which provided the principal source of labour for their seasonal production campaign (November and February). These people found employment for the remainder of the year on local farms. In the 1980s the town became a commuter town and this resulted in a shift in the social make up of the population. Consequently, there was a significant increase in the level of odour complaints made about the processing facility. The economics of mitigating the odours were prohibitive and the site ceased production.

Similar perception differences can be found with shifting populations away from towns/cities to rural location. Activities giving rise to countryside odour, e.g. muck-spreading, are generally more acceptable to those to who live there and are accustomed to the odour and accept it as part of the environment. However such odours may well cause offence at a lower exposure level to "townsfolk" who have recently moved to the countryside.

### **2.1.5** Attributes of odours

Every odour sensation comprises a number of attributes. These attributes can be summarised as (Valentine and North, 1980):

- Hedonic tone or quality - pleasantness and unpleasantness.
- Intensity (or strength) - faint to strong.
- Recognition - reference can be made to characteristics odour descriptions and it may be possible to identify key odour components.

There are a number of anomalies with the above attributes. For example:-

- An odour may be pleasant when weak, unpleasant when strong.
- An odour may have one quality when first perceived, but another if persistent.

The concept of detectability is used to take account of these anomalies. The unit of detectability is the dilution to threshold value (i.e. the dilution at which there is a 50% probability of odour detection). This is typically described as an odour unit or as the Threshold Odour Number (TON).

In situations where an odour emission comprises a single odorant, the odour detection threshold can be expressed in terms of a concentration (mass per unit volume). To validate the odour concentration, the detection threshold value must be calculated numerous times so that it is as close to the true (actual) odorant threshold value as possible. For the vast majority of odorants there is a high level of uncertainty with the detection threshold value. This is because the published data has been generated by non standard olfactometric techniques. Where the odour emission comprises a mixture, the odour concentration should be expressed in terms of odour units.

International standard definition of an odour unit.

*"The amount of odorant(s) that, when evaporated into 1 cubic metre of odourless gas at standard conditions, causes a physiological response from a panel (detection threshold) equivalent to that elicited by 40 ppb (0.123 mg/m$^3$ at STP) of n-butanol (CEN TC264/WG2)".*

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## 2.2 Regulation

The IPC license system was established in 1994 along with a formal complaint system was established. The EPA has produced annual reports from 1996, most of the complaints made since then relate to odour (58% to 78%). The number of complaints received since commencement of the EPA is presented in Table 2.1. below. The rendering of animal by-products, followed by the fiber board, slaughtering and pharmaceutical industries had the highest number of complaints (EPA 1997,1998, 1999, 2000, 2001, 2002).

Under IPC licensing, activities such as rendering and other facilities are required to assess odours generated on site and to carry out whatever work is necessary to abate the odours. Improved negative air pressure and odour abatement equipment is being installed at some of these facilities. However, good management practices and proper operation of the abatement equipment are also of critical importance.

Continuing improvement in relation to the issue of odour is expected as the EPA conducts audits and more routine visits, and it is hoped to continue the reduction of complaints through proactive enforcement and good management.

| Year | Total | Odour | % of complaints relating to Odour |
|---|---|---|---|
| 1996 | 466 | 279 | 60 |
| 1997 | 1026 | 722 | 70 |
| 1998 | 1897 | 1475 | 78 |
| 1999 | 1733 | 1330 | 77 |
| 2000 | 1480 | 947 | 64 |
| 2001 | 1737 | 1008 | 58 |
| 2002 | 1273 | 779 | 61 |

**Table 2.1. Odour Complaints (Source EPA annual reports 1996 -2002)**

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The Regulators of IPC processes must ensure that the plant operator uses Best Available Techniques (BAT) to prevent, or where not practicable by such means, to minimise and render harmless all releases to the environment (in the case of processes remaining under IPPC control this only relates to emissions to air). The definition of harm is important to the BAT requirement. Harm can be defined, amongst other things, as offence caused to any sense of man. In the context of this report, the offence is that caused by odour nuisance .

Guidance to Local Authorities (LAs) on how to determine offensiveness has been given by the Department Of Environment (DoE, 1995):

> *"Assessment of offensiveness should take account of the nature of the odour, the frequency with which it arises, and its persistence. Where offensive odours are perceived, the Local Authority should examine the process and proceed as for complaints. Local authorities should bear in mind that dispersal of odour may, from time to time, be adversely affected by temporary meteorological conditions."*

### 2.2.1 Odour measurement

The exposure of the population to a particular odour consists of two factors; the concentration and the length of time that the population may perceive the odour. By definition, 1 ou/m$^3$ is the detection threshold of 50% of a qualified panel of observers working in an odour-free laboratory using odour-free air as the zero reference. The recognition threshold is generally about five times this concentration (5 ou/m$^3$) and the concentration at which the odour may be considered a nuisance is between 5 and 10 ou/m$^3$ (Warren Spring, 1980) based upon Hydrogen Sulphide analysis from WWTP in the UK.

### 2.2.2 Licence limits

IPC license conditions relating to odour emissions reflect local conditions for example conditions have included direct emission limits for the total odour emissions from a particular source or activity.

These come in a number of forms. An example of a generic condition is:

*"The licensee shall ensure that all operations on-site shall be carried out in a manner such that air emissions and/or odours do not result in significant impairment of, or significant interference with amenities or the environment beyond the site boundary."*

Indirect control for the total odour emissions from a given site is achieved by specifying emission limits of common odorants. These come in a number of forms and an example of an Authorisation condition of this type is:

- TA Luft
- BATNEEC Guidance Notes for Animal By-products and Intensive Agriculture.

Condition 3: "*The following concentration in emissions to air shall not be exceeded*:

- *Ammonia 50 ppm v/v*
- *Amines and Amides 5 ppm v/v*
- *Organic and inorganic sulphides 5 ppm v/v*"

The U.S. Occupatioal Safety and Health Administration (OSHA) established an acceptable ceiling concentration of 20ppm with a maximum concentration of 50 ppm for 10 minutes for Hydrogen Sulphide. The U.S.National Institute of Occupational Safety and Health (NIOSHA) has set a maximum recommended exposure of 10ppm for 10 minutes. (ATSDR 2002) It must be recognised that compliance with emission limits of prescribed substances does not necessarily mean that there is no offensive odour.

### **2.2.3** Monitoring

These conditions come in a number of forms. An example of a generic condition is: *"Condition Y: Within (N) months of the issue of this license, a scheme of monitoring for offensive odours arising from operations on the site and in the post operational phase, shall be devised by the operator and agreed in writing with the Agency. The scheme shall cover such matters as the method of assessment to be employed, identification of personnel specified to carry out monitoring details of guidance, instruction and training given to specified personnel, minimum frequency of monitoring,, liaison with the EPA, the period over which the monitoring will take place, monitoring points on and off the site and record keeping."*

License conditions can be used as a valuable tool to impose periodic monitoring of plant operation impacts. However, since odour events are typically of short duration, the effectiveness of this approach is somewhat limited. Any odour events that do occur may well be missed by the relatively infrequent monitoring of emissions. Alternative odour assessment criteria, related to odour dispersion modelling studies may also be defined.

An example of such a criterion is:
5 ou/m$^3$ as a 98th percentile of hourly means.

### 2.2.4 Other European systems

.In the Netherlands odour assessment criteria and odour nuisance standards relating to dispersion modelling studies are dealt with by two documents:-

- The Nederlandse, Emissie Richtlijn (NER, Dutch Emission Guideline).
- The Nota Stankbeleid (note on odour policy).

The NER is aimed at processes which generate odour, and values in the guideline are used as a prescriptive approach for environmental permits granted to developments. The standards given in the NER are summarised below:

Type of source Statistic Concentration

- For existing continuous sources in populated areas 98th percentile 1 ou/m$^3$
- For existing fluctuating sources in populated areas 99.99th percentile 10 ou/m$^3$
- For new continuous sources in populated areas 99.5th percentile 1 ou/m$^3$
- For new fluctuating sources in populated areas 99.99th percentile 10 ou/m$^3$
- For new and existing studies in unpopulated areas 95th percentile 1 ou/m$^3$

Compliance with the relevant impact concentration can be tested by collecting gas samples from the site, determining the odour concentration by dynamic dilution olfactometry and using dispersion modelling (e.g. ADMS) to predict the impact

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concentration under the relevant statistical condition. There are no guidelines on the extent of the initial sampling required to provide the odour emissions data, however it is unlikely that compliance will need to be verified if the emissions from the site do not give rise to complaints. If complaints are received then a single measurement campaign should provide sufficient data to check compliance.

If sufficient odour monitoring data have been gathered, dispersion modelling should be able to cope with a number of point/diffuse sources to allow assessment with the NER limits.

## 2.3 Hydrogen Sulphide

### 2.3.1 Chemical and Physical Properties

Hydrogen sulphide is a flammable colourless gas with the characteristic odour of rotten eggs. It burns in air with a pale blue flame and, when mixed with air, its explosive limits are 4.3% to 46% by volume. Its auto ignition temperature is 260°C. The relative molecular mass of hydrogen sulphide is 34.08. Its density is 1.5392 g/litre at 0°C and 760 mm. The ratio density of hydrogen sulphide compared with air is 1.19. One gram of hydrogen sulphide dissolves in 187 ml of water at 10°C, (calculated from West, 1977—78). It is also soluble in alcohol, ether; glycerol, and in solutions of amines, alkali carbonates, bicarbonate and hydrosulphides. The vapour pressure of hydrogen sulphide is 18.75 X $10^5$ Pa at 20°C and 23.9 X $10^5$ Pa at 30°C. Its melting point is 85.5°C and its boiling point is 60.3°C (Macaluso, 1969; Windholz, 1976). Hydrogen sulphide can undergo a large number of oxidation reactions, the type and rate of the reaction and the oxidation products depending on the nature and concentration of the oxidizing agent. The principal products of such reactions are sulphur dioxide, sulphuric acid, or elemental sulphur. Aqueous solutions of chlorine, bromine, and iodine may react with hydrogen sulphide to form elemental sulphur.

Hydrogen sulphide dissociates in aqueous solution to form 2 dissociation states involving the hydrosulphide anion (HS) and the sulphide anion (The pKa in 0.01—0.1 mol/litre solutions at 18°C is 7.04 for HS and 11.96 for S. At the physiological pH of 7.4, about one-third of the total sulphide remains as the undissociated acid and about two-thirds as the HS ion. The undissociated hydrogen sulphide in solution is in dynamic equilibrium at the air-water interface with gaseous hydrogen sulphide (National Research Council, USA, 1977).

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The methylene blue colorimetric method has acceptable specificity, accuracy, and sensitivity for hydrogen sulphide determinations, and is generally recognized as a standard analytical procedure. It has been used successfully in automatic continuous monitoring, but sophisticated maintenance facilities and highly trained technicians are required for this method. Gas chromatography, coupled with flame photometric detection is an alternative method for hydrogen sulphide determination, either as a laboratory method or for continuous monitoring in stationary field settings. Most of the direct-reading methods of hydrogen sulphide determination in the occupational environment are susceptible to various forms of interference. However, methods employing chemical detector tubes appear to be useful in occupational settings, where hazardous levels of hydrogen sulphide can occur. Under these conditions, reliability and accuracy compensate for a certain lack of specificity.

### 2.3.2 Atmospheric Chemistry

The atmospheric chemistry of hydrogen sulphide and other sulphur compounds involves chemical and photochemical oxidation reactions of emissions from both natural and man-made sources. The eventual oxidation products are sulphuric acid ($H_2SO_4$) and/or sulphate ion ($SO_4$). There have been relatively few studies of the persistence and conversion of hydrogen sulphide under atmospheric conditions. Krasovitskaja and her co-workers (Krasoitkaa *et al.*, 1965) studied the relationship between concentrations of hydrogen sulphide, sulphur dioxide, carbon monoxide, and hydrocarbons, and the distance from their industrial sources. Hydrogen sulphide concentrations dropped by a factor of 2 between the immediate neighbourhood of the source and a 2.5 km radius. A further decrease in concentration ranging from 300 up to a factor of $10^8$ occurred between the 2 km and 20 km radius. These decreases were, in general, greater than those observed for any of the other pollutants measured. Andersson *et al.* (1974) reported studies concerning the photolysis of hydrogen sulphide and its reaction with sulphur dioxide, as well as its reactions with atomic and molecular oxygen and with ozone.

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Junge (1963) calculated that the residence time of hydrogen sulphide was approximately 1.7 days in the presence of an ozone level of 0.05 mg/m$^3$. A similar residence time was estimated by Katz (1977) using data from the global budget of the sulphur cycle presented by Kellogg *et al.* (1972). Robinson & Robbins (1970) found a residence time in relatively clean air of about 2 days, compared with only about 2 h in a polluted urban atmosphere.

Considerably lower values than those of the previously mentioned investigators, based on the global sulphur budget, have been presented by Granat *et al.* (1976), on the basis of a very much lower release of sulphur compounds from the biological decay of organic matter from land and sea

### 2.3.3. Sources of Hydrogen Sulphide

Hydrogen sulphide is one of the principal compounds involved in the natural cycle of sulphur in the environment. It occurs in volcanic gases and is produced by bacterial action during the decay of both plant and animal protein. It can also be produced by bacteria through the direct reduction of sulphate. Significant concentrations of hydrogen sulphide occur in some natural gas fields and in geothermally active areas. Hydrogen sulphide can be formed whenever elemental sulphur or certain sulphur-containing compounds come into contact with organic materials at high temperatures. In industry, it is usually produced as an undesirable by-product, though it is an important reagent or intermediate in some processes. Hydrogen sulphide occurs as a by-product in: the production of coke from sulphur-containing coal, the refining of sulphur-containing crude oils, the production of carbon disulfide, the manufacture of viscose rayon, and in the Kraft process for producing wood pulp.

#### 2.3.3.1 Natural Sources

Hydrogen sulphide is one of the principal compounds involved in the natural sulphur cycle in the environment (National Research Council, USA, 1979). It occurs in volcanic gases as shown in Fig. 2.1.

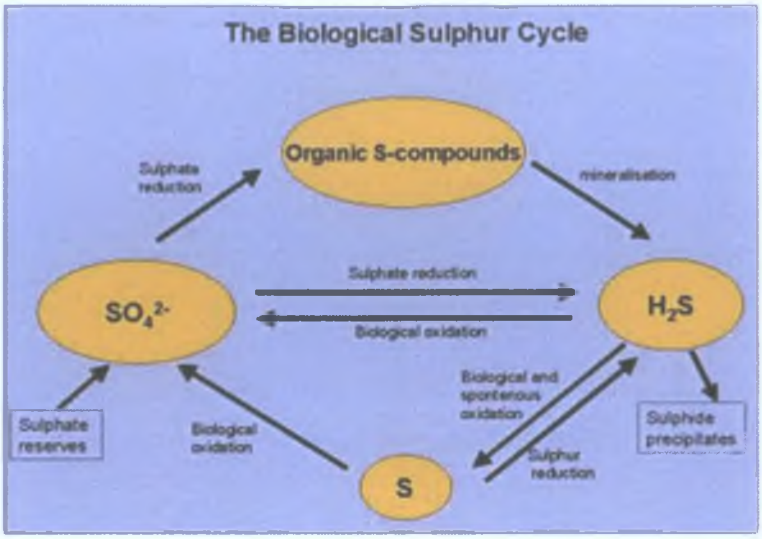

**Figure 2.1 The Biological Cycle: source Cooper *et al*, 1976**

The Sulphur cycle is produced by bacterial action during the decay of both plant and animal protein (Cooper *et al.* 1976). Many bacteria, fungi, and aetinomycetes release hydrogen sulphide into the environment during the decay of compounds containing sulphur-bearing amino acid and in the direct reduction of sulphate. The heterotroph *Proteus vulgaris* is an example of a common bacterium that produces hydrogen sulphide, when grown in the presence of protein (National Research Council, USA, 1979).

The reduction of sulphate to hydrogen sulphide can be accomplished by members of 2 genera of anaerobic bacteria, Desulfovibrio and Desulphotormaculiuim. The organic substrates for these organisms are usually short chain organic acids that are provided /by the fermentative activities of other anaerobic bacteria or more complex organic material. Hence, hydrogen sulphide production can be expected in conditions where oxygen is depleted, organic material is present, and sulphate is available (National Research Council, USA, 1979).

From a microbiological point of view, the production of hydrogen sulphide is balanced by processes involving a variety of bacteria, found in soil and water, that can oxidize hydrogen sulphide to elemental sulphur. Among these are the filamentous bacteria, Beggiatoa and Thiothrix. Photosynthetic bacteria belonging to the families Chromatiaceae and Chlorobiaceae oxidize hydrogen sulphide to elemental sulphur and sulphate in the presence of light and the absence of oxygen. Reduced sulphur compounds are also oxidized in nature by members of the genus Thiobacillus. The end result of this oxidative activity is the production of sulphate which, once formed, is extremely stable to further chemical activity in nature (National Research Council, USA, 1979). As a result of these various biogeochemical processes, hydrogen sulphide occurs in and around sulphur springs and lakes and is almost continuously present as an air contaminant in some geothermally active areas.

### 2.3.3.2.Sources Associated with Human Activity.

There are various circumstances under which naturally occurring hydrogen sulphide is released by human activity. For example, hydrogen sulphide occurring in association with natural gas and/or crude oil deposits in some areas may be released during extraction and drilling operations. The sulphur content of crude oils ranges from 0% to 5% and some natural gas deposits have been reported to comprise up to 42 % hydrogen sulphide (Espach, 1950). Coals can contain sulphur levels of up to 80 g/kg and, occasionally, conditions arise in which hydrogen sulphide is formed within such deposits. Thus, special precautions must be taken in some mining operations as well as in the drilling and extraction of natural gas and crude oils with significant sulphur content. Hydrogen sulphide can also be released by activities surrounding the development and use of geothermal resources. At the Cerro Prieto geothermal power generating plant in Baja California, Mexico, for example, hydrogen sulphide levels are sufficiently high to necessitate special ventilation to protect electrical systems, and alarms for the protection of personnel (Mercado, 1975).

During industrial operations, hydrogen sulphide can be formed whenever elemental sulphur or certain sulphur-containing compounds come into contact with organic materials at high temperatures. It is usually produced as an undesirable by-product, though it is also used as an important reagent or desirable intermediate compound in some industrial processes such as the manufacture of sulphides, sodium hydrosulphide, and various organic sulphur compounds. Examples of processes in which hydrogen sulphide occurs as a by-product include the production of coke from sulphur-containing coal, the production of carbon disulphide, the manufacture of viscose rayon in the Kraft process for producing wood pulp (Macaltjso, 1969) and sulphur extraction by the Frasch process.

In refining sulphur-containing crude oils, about 80% -90% of the divalent sulphur compounds of hydrogen and carbon are converted to hydrogen sulphide. Both the hydrogen sulphide produced and that occurring in other industrial, geothermal, or natural gas streams can be recovered by one of a number of processes that can be classified as either absorption—desorption processes or processes involving oxidation to oxides or to elemental sulphur. The bulk of hydrogen sulphide recovered in industrial processes is used to produce elemental sulphur or sulphuric acid (Macaltjso, 1969).

As in the natural environment, hydrogen sulphide can be generated by bacterial action in industrial or community settings in malodorous and sometimes dangerous amounts. In some countries, such as India and Sri Lanka, hydrogen sulphide is produced in the process by which coconut fibres are separated from the husk. This procedure involves the decomposition of the husks in hallow ponds. The hydrogen sulphide is produced as a result of microbiological decay processes.

### **2.3.4** Environmental levels and exposures

Though concentrations of hydrogen sulphide in urban areas may occasionally be as high as 0.050 mg/m$^3$ (0.033 ppm) with averaging times of 30 minutes – 1 hour, they are generally below 0.0015 mg/m$^3$ (0.001 ppm). Peak concentrations as high as 0.20 ng/m$^3$ (0.13 ppm) have been reported in the neighbourhood of point sources. In a geothermal area, 1h mean concentrations of up to 2 mg/m$^3$ (1.4 ppm) have been observed. When hydrogen sulphide was accidentally released in an incident in Pose Rica, Mexico, in 1950, the number of deaths that followed indicated that exposure levels probably

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exceeded 1500—3000 mg/m$^3$ (1000—2000 ppm). It is believed that workers are not usually exposed to hydrogen sulphide concentrations above the occupational exposure limits of 10—15 mg/m$^3$ (7—10 ppm) (8-h time-weighted average) adopted by many governments. There are, however, numerous reports of accidental exposures to concentrations that have ranged from 150 mg/m$^3$ (100 ppm) to as high as 18 000 mg/m$^3$ (12 000 ppm). Such exposures to hydrogen sulphide have resulted either from leaks in industrial gas streams containing high levels of hydrogen sulphide or from the slow, insidious accumulation of hydrogen sulphide in low-lying areas. The second case may arise when hydrogen sulphide is generated from such sources as sewage disposal plants and cesspools.

### **2.3.5** Effects on animals

In experimental animals, the effects of high doses of hydrogen sulphide and high doses of cyanide are very similar. Cyanide inhibits the enzyme cytochrome c oxidase [EC 1.9.3.1] a, thereby interfering with tissue use of oxygen to the point where metabolic demands cannot be met. Hydrogen sulphide also exhibited an inhibitory action on a purified preparation of *cytochrome c oxidase*. Results of studies on a number of animal species including canary, rat, guinea pig , cat, dog, and goat showed that inhalation of hydrogen sulphide at a concentration of 150—225 mg/m$^3$ (100—150 ppm). Signs of local irritation of eyes and throat after many hours of exposure; at 300—450 mg/m$^3$ (200—300 ppm), eye and mucous membrane irritation appeared after 1 h inhalation and slight general effects after prolonged inhalation; at 750—1050 mg/m$^3$ (500—700 ppm), local irritation and slight systemic signs appeared within 1 h and death after several hours; at 1350 mg/m$^3$ (900 ppm), serious systemic effects appeared in less than 30 m and death within 1 h; at 2250 mg/m$^3$ (1500 ppm), collapse and death occurred within 15—30 minutes and, at 2700 mg/m$^3$ (1800 ppm), there was immediate collapse with respiratory paralysis, and death. There is little information on the effects on experimental animals of long-term, low-level exposure to hydrogen sulphide gas.

### 2.3.6 Effects on man

2.3.6.1 General toxicological considerations

Hydrogen sulphide is both an irritant and an asphyxiant gas. Its direct irritant action on the moist tissues of the eye produces keratoconjunctivitis, known as "gas eye". When inhaled, hydrogen sulphide exerts an irritant action throughout the entire respiratory tract, although the deeper structures suffer the greatest damage. A consequence may be pulmonary oedema. At concentrations of 1500—3000 mg/m$^3$ (1000—2000 ppm), hydrogen sulphide gas is rapidly absorbed through the lung into the blood, which initially induces hyperpnoea (rapid breathing). This is followed by respiratory inactivity (apnoea). At higher concentrations, hydrogen sulphide exerts an immediate paralysing effect on the respiratory centres. Death due to asphyxia is the certain outcome, unless spontaneous respiration is re-established or artificial respiration is promptly provided. This sequence of events represents the most important toxic effect of hydrogen sulphide. Acute hydrogen sulphide intoxication can be defined as the effects from a single exposure to massive concentrations of hydrogen sulphide that rapidly produce signs of respiratory distress. Concentrations exceeding about 1500 mg/m$^3$ (1000 ppm) produce such acute effects. Sub acute hydrogen sulphide intoxication is the term applied to the effects of continuous exposure for up to several hours to concentrations ranging from 150 to 1500 mg/m$^3$ (100—1000 ppm). In this range of exposure, eye irritation is the most commonly observed effect.

However, some reports have indicated that the threshold for eye irritation occurs after several hours of exposure to hydrogen sulphide at levels of 16—32 mg/m$^3$ (10.5—21.0 ppm). Pulmonary oedema may be a more important and potentially fatal complication of sub acute hydrogen sulphide intoxication. Chronic intoxication is a largely subjective state characterized by fatigue and believed by some to be a consequence of intermittent exposure to hydrogen sulphide concentrations of 75—150 mg/m$^3$ (50—100 ppm). Not all research workers accept the existence of such a condition.

The characteristic "rotten egg" odour of hydrogen sulphide is well known. The threshold of perception of this odour varies considerably depending on individual sensitivity, but, under laboratory conditions, it ranges from 0.0008 to 0.20 mg/m$^3$ (0.0005—0.13 ppm).

Above about 225 mg/m$^3$ (150 ppm), the gas exerts a paralysing effect on the olfactory apparatus, thus neutralising the value of its odour as a warning signal. At these concentrations, the odour of the gas has been reported to be sickeningly sweet.

### 2.3.6.2 Occupational exposure

Exposure to hydrogen sulphide in high concentrations occurs in numerous occupations. Workers in the oil, gas, and petrochemical industries are occasionally exposed to hydrogen sulphide in concentrations sufficient to cause acute intoxication. In one survey of the petrochemical industry, among 221 cases of hydrogen sulphide poisoning, the overall mortality was 6% and a high proportion of victims exhibited neurological signs and symptoms. Forty percent of all cases required some form of respiratory assistance; 15% developed pulmonary oedema. Persistent sequelae following acute intoxication have been reported among workers in a number of occupations including sewer workers, chemical plant employees, farmers, whale-oil workers, and laboratory attendants. Most victims who develop sequelae experience a state of unconsciousness during acute phase of their illness. However, sequelae following acute intoxication without unconsciousness have also been reported.

### **2.3.6.3** Exposure of the general population

Several episodes of general population exposure to hydrogen sulphide have been reported. The effects of such exposure have ranged from minor nuisance to serious illness and death. In a small community adjacent to an oilfield installation, large quantities of hydrogen sulphide were released into the air when an oilfield flare malfunctioned. Three hundred and twenty persons were hospitalized, 22 of whom died. Nine exhibited conditions of pulmonary oedema. Four victims developed neurological sequelae. The air levels of hydrogen sulphide were not measured. A community of 40 000 people, located in the vicinity of a large geothermal field, was exposed in some areas to hydrogen sulphide levels in air (measured on a continuous basis over a 5-month period) exceeding 0.08 mg/m$^3$ (0.05 ppm), for, on average, 35% of the time. Although fatal cases of hydrogen sulphide intoxication associated with improper ventilation in geothermal steam-heated dwellings in this area were occasionally reported until 1962, the major problem has been the nuisance caused by the odour of the gas. In a moderately sized community, hydrogen sulphide was released from a small industrial waste lagoon resulting in a 1-h average concentration of hydrogen sulphide in air of 0.45 mg/m$^3$ (0.3 ppm). Complaints were mostly related to the odour of hydrogen sulphide gas. However, the severity of complaints of nausea, vomiting, headache, loss of appetite, and disturbed sleep exceeded the mere nuisance level.

No community studies of the long-term, low-level effects of hydrogen sulphide exposure have been reported. The sense of smell for Hydrogen Sulphide is readily fatigued by continuous exposure (Shy 1978)

### 2.6.3.4 Evaluation of health risks

Hydrogen sulphide in ambient air in concentrations of the order of the odour threshold has not been shown to have any significant biological activity in man or animals. In controlled laboratory studies, the odour, threshold for hydrogen sulphide has been reported to range from 0.0008 to 0.20 mg/m$^3$ (0.0005—0.13 ppm). Little information is available on the odour detection limits for hydrogen sulphide either under experimental field conditions or in the ambient air.

It is considered that a level of 0.008 mg/m$^3$ (0.005 ppm) averaged over 30 m should not produce odour nuisance in most situations. In the occupational setting, the earliest toxic response appears to be irritation, which has been reported to occur at 16—32 mg/m$^3$ (10.5—21.0 ppm) after several hours exposure. The occupational exposure guidelines for hydrogen sulphide recommended by the Task Group included the adoption of a level of 10 mg/m$^3$ (7 ppm) as a time-weighted average value together with a short-term exposure limit of 15 mg/m$^3$ (10 ppm), the latter to be determined as a 10-m or less, average value.

## 2.4 Principal methods of controlling odorous gases

### 2.4.1 Introduction

The author looked at numerous methods of abating or controlling odour nuisance and in particular what methods could be used in Aughinish Alumina Ltd (AAL )

To assist in the choices of abatement systems the author used as a rule of thumb for guidance

- Odour source
- Consideration should be whether the odour can be avoided by better containment
- Concentrations and volume flow rates
- The temperature of the gas
- Moisture content
- Chemical composition
- Disposal of waste products

In this section the author outlines the following end-of –pipe abatement techniques:

- **Adsorption** e.g. using Activated carbon -zeolite – alumina
- **Dry chemical scrubbing** e.g. solid phase impregnated with chlorine dioxide or permanganate
- **Biological Techniques** e.g. Soil bed bio filters - Peat/heather, wood bark, compost bio filters, Bio scrubbers
- **Absorption (Scrubbing)** e.g. using Packed towers
- **Incineration** e.g. Plant boiler - Thermal – Catalytic
- **Other techniques** e.g. masking agents, counteractants, landscaping, separation distances, dilution, condensation, plasma technology, catalytic iron filters and in stack abatement technique

### 2.4.2 Containment

Some processes are easily contained, whilst others are not, e.g. batch rendering, landfill sites, effluent treatment etc. The first step in odour abatement is to examine the process and to maximise the containment of total odour. The next step is to localise process odours to reduce the volume of highly odorous gas. Containment of highly odorous process gases may reduce the capital and operation costs.The enclosure device must collect and vent pollutants to an abatement process. They must have a minimum of 4 room changes per hour for industrial settings (OSHA). The pollutant concentration concentration must not exceed 10% of the LEL inside the enclosure.(EPA 2002) Depending on the design and the concentration of the gases it is estimated that local concentrations inside enclosures can vary by factors of 1 to 10 (Worrall 1997)

### 2.4.3 Adsorption

Adsorption is an appropriate odour abatement technology for gas streams containing low odour concentrations. Typically, abatement efficiencies range from 90 to 99.9% removal the efficiency depends on the chemical adsorbed. Depending on the nature of the chemical absorbed, the post abatement residual odour can be as low as 100 to 400 ou/m$^3$

The process of adsorption is a heterogeneous reaction in which gas molecules are captured and retained on a solid surface (the adsorbent). Some adsorbents preferentially adsorb specific chemical species and hence, odorous components can be removed from gaseous streams. For example, it is common practice in the water industry to use activated carbon to prevent the release of hydrogen sulphide into the environment. Once the activated carbon becomes saturated (i.e. all its adsorption sites are full) it is usually replaced and sent for disposal. At present there are three major types of adsorber system:

- Fixed bed unsteady-state adsorbed - contaminated gas is passed through a stationary bed of adsorbent - due to its cost, this type is the most commonly used in the odour abatement market.
- Fluidised bed adsorber - contaminated gas passes through a suspension of adsorbent;

- Continuous moving bed adsorber - adsorbent falls by gravity through a rising stream of contaminated gas.

For odour issues fixed bed adsorbers are by far the most common, largely because they are the cheapest of the three types (Cha, 1999).

Adsorption occurs when there is mass transfer of molecules from the bulk of gas to the gas solid interface and then diffusion through the pores of the adsorbent until the molecule is finally adsorbed onto an internal surface. There are two types of adsorption - physical and chemical.

***Physical adsorption*** - adsorbed molecules (the adsorbate) are held to the adsorber surface by Van der Waals forces (molecule-to-molecule interactions). This type of adsorption is typically used for removal of volatile organic compounds (VOCs). The physical sorption capacity of activated carbon for Hydrogen Sulphide is about 10kg/m$^3$ (Turk *et al* .1989)

***Chemical adsorption*** - compounds are impregnated onto the adsorbent to react with specific odorous compounds, e.g. carbon can be impregnated with caustic to remove hydrogen sulphide and with citric acid to remove ammonia. The most important consideration when designing an adsorber system is the type of adsorbent required. This is largely dependent on the nature of the gaseous stream. Retention time is very important to achieve good removal efficiency, a 99% removal efficiency can be achieved with a residence time of 6.5 seconds (Le CLoirec,1995)

Activated carbon can be modified in one of two ways:

- It can be impregnated with chemicals to enhance adsorption capacity by reaction.
- The size of the pores within the activated carbon can be modified.

It should be noted that the greater the extent of modification made to the activated carbon, the greater the resulting cost.

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The first two have a similar capacity to carbon and are often used to dehydrate gas streams. Metal oxides, such as activated alumina, are mainly used for the preferential adsorption of polar molecules such as carbon dioxide and sulphur dioxide. Greater than 90% efficient can be used for removing odours of known composition and for post incineration if necessary

### **2.4.3.1** Adsorptive capacity

The adsorptive capacity of the adsorbent depends on a number of factors. Adsorption is dependent on gas molecules reaching the internal pores of the adsorbent, hence the significant factors are

- Retention in the adsorption bed
- Concentration of the adsorbate around the adsorbent;
- The surface area of the adsorbent;
- The volume of pores in the adsorbent which are of appropriately sized;
- The particular characteristics of the adsorbate surface (weight, electrical polarity and shape);
- The properties of the adsorbent surface (polarity and shape of pores).
- The equilibrium dynamics, e.g. competition of gas components for a place on the adsorbent.

For the removal of odorous gases, ambient temperatures of about 15-40°C are generally recommended. If the temperature is too high desorption may occur, and if too low the rate of adsorption reduces considerably. Adsorption also increases with high partial pressures. Humidity should be kept below 50% because adsorptivity is reduced at higher humidity (water is preferentially adsorbed rather than the odorous compounds). For impregnated adsorbents, e.g. activated carbon coated with citric acid, the adsorptive process relies on chemical reaction. Turk *et al.*(1989) observed that an unimpregnated activated carbon used in conjunction with a small side stream of ammonia gas would remove three times more Hydrogen Sulphide. A retention time of 1 second in the adsorption is required as a general rule in odour treatment applications. Le Cloirec (1995) obtained 99% removal efficiency for Hydrogen Sulphide (concentration 7 to

70ppmv) in WWTP emissions applying an AC adsorber at a gas residence of 6.5 seconds. Adsorption has been found to be more effective at humidity close to 100%. The high humidity is required to allow odorous gases to absorb into the water layer on the adsorber surface. Once adsorbed into the water layer the compounds react with the impregnated adsorbent.

If the pressure drop across the bed is too high, dusting and abrasion of the adsorbent particles and channelling due to their re-arrangement may occur. If the additional pressure drop can be tolerated, two beds in series give a high degree of removal and, towards the end of the life of the first bed; the second bed provides additional insurance against premature or accidental bed penetrations.

When the concentration of the odorous components in the discharge stream of the adsorber becomes unacceptable, the adsorbent will need to be replaced or regenerated (usually regenerated by steam). In the majority of cases, spent beds of adsorbent are usually replaced because of the additional capital and operating costs of installing a regeneration system. An alternative is to use a number of carbon filters in series. They are designed to allow each carbon filter to be interchangeable, thus optimising the efficiency of the abatement system as a whole.

Odorous gases can be passed through beds of activated carbon to remove odours. Some limits exist with humidity and the particular size of the pore in the carbon. However this system involves high investment and high running costs (J. Myung Cha,1999)

#### 2.4.3.2 Problems encountered with adsorption for odour control

- Particulate material in the gas stream can cause problems and therefore dust filters may need to be fitted up-stream.
- Odour will breakthrough once the adsorbent has been saturated.
- The differing adsorption rates for different chemical compounds in a gaseous mixture may cause break through before the adsorbent is fully saturated.
- If the adsorbent is recycled on site it may, after many cycles (adsorption - desorption - adsorption etc.), lose its ability to be regenerated *in situ*. When this

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occurs external reactivation (usually by the supplier) or replacement (spent carbon is typically disposed of by landfill or incineration) is required.

### 2.4.4 Dry Chemical Scrubbing

Recently, dry chemical scrubbers have come onto the odour abatement market. These typically consist of an oxidising chamber and a polishing stage, the functions of which are:

1. Oxidising chamber - oxidising material (e.g. chlorine dioxide, potassium permanganate etc.) impregnated on a support material. The odorous gas passes up through the oxidising chamber where it is absorbed and then oxidised to non-odorous by-products.
2. Polishing Stage - comprises activated carbon which is used to remove any un-oxidised odorous compounds

Dry chemical scrubbers are ideal for extremely low flow, relatively high concentration streams. They can be purchased as stand alone systems so that a unit can be installed next to the source, avoiding the need for complicated ducting systems, hence, the overall cost may be lower.

Dry chemical scrubbers are being used by the water treatment companies to treat the odour from storage tanks and wells.

#### 2.4.4.1 Problems encountered

- There may be emission of oxidised products, e.g. chlorine.
- Washout of oxidising products is possible, e.g. potassium permanganate, which is best suited to a proces with a pH of 5 to 7 and this will also reduce the usage of potassium permanganate Pisarezyk and Rossi (1992) .
- The lifespan of the oxidising media may be limited.
- Specialist labour is required for media replacement.
- There is potential for low odour removal effectiveness because of a high residual chemical odour.
- Not particularly suitable for high gas flow rate.

### 2.4.5 Biofilters

It is a well established principle that certain odorous compounds, particularly those from 'natural' processes, can be metabolised by naturally-occurring micro-organisms and fungi. These micro-organisms are reasonably robust provided that there is a constant supply of carbon and oxygen. Typically, after a period of adaptation, the microbial population will self select itself to degrade the defined odorous gas stream.

This phenomenon is widely used as the basis for odour control devices. High efficiency (>99%) of odour reduction with minimal secondary pollution can be achieved at relatively little cost providing care is taken to establish and maintain the viability of the active biological species. The residual post abatement odour concentration from an adequately sized bio filter where the feed stream variation is relatively low can be of the order of 100 to 400 ou/m$^3$ depending on the bio- filter medium used. There are two basic types of bio-oxidation equipment:

Bio filters

- Soil based.
- Non soil based.

Bio scrubbers

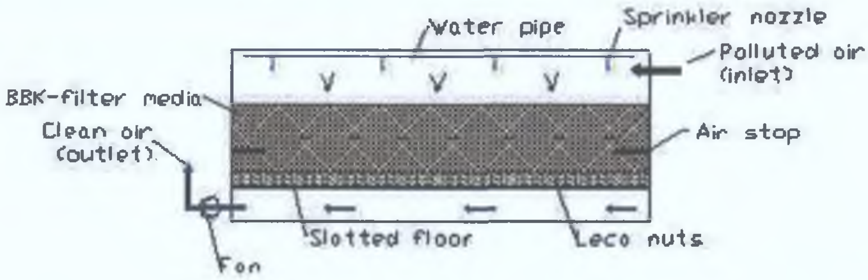
The following sections describe the two types of bio-oxidation equipment in more detail.

#### **2.4.5.1** Soil biofilters

The media has a very high surface area to support the microbes and works under a low pressure system. Bio-filters are built so that the polluted air is led through the filter media. Often the polluted air is mixed with air from room-ventilation before entering the top of the bio- filter. As the air passes down through the filter media, specific micro-organisms will decompose the odorous compounds into $CO_2$ and water. The detention time may vary, but it is typically 25-35 seconds depending on the complexity of the odorous compounds.

A soil bio-filter consists of a moist layer of porous soil supporting a diverse and rich supply of bacteria and fungi, underlain by a network of perforated pipes through which the odorous air is passed. The odorous air is passed up through the soil and the microbes oxidise the odorous compounds in the air to less noxious/odorous substances. The treated air stream is then discharged.

**Fig 2.2: Bio filter (source www.bbk.dk)**



As with non-soil bio-filters, soil bio-filters require water and a suitable matrix on which biological organisms can exist. Soil bio - filters have a more varied biological population which exists in a less controlled environment than non-soil bio-filters and thus require relatively long residence times. They therefore tend to be larger than non-soil bio-filters. Hence, soil bio-filters are best suited to applications where there is a large amount of free land.

The contaminated air is usually fed to the bio-filter by means of perforated pipes set at right angles to the header pipe. The perforated pipes should be laid in a continuous layer of coarse gravel which will act as distributor and allow the contaminated air to flow uniformly through the bio filter. A soil depth of one metre is usually recommended and the soil should be open textured with a high organic content, e.g. sandy soil. Sometimes it is necessary to separate the air distribution system into sub systems to ensure uniform distribution if the bed consolidates non uniformly.

The residence time in a soil bio-filter depends on the process and odour concentration, but it typically varies between 3-5 minutes. In principle, the technique is suitable for a wide range of applications providing that there is sufficient land space available. Odour removal efficiencies may be as high as 99%, but typically manufacturers guarantee 95%.

Soil based bio-filters should be irrigated (10 litres per square metre of bio- filter per day) to ensure that the soil remains moist, particularly during periods of low rainfall.
Day to day activities should include visual examination of the bed for cracks or holes where untreated gas may be escaping. The escape of untreated gas can usually be detected by scorched vegetation in the vicinity of the crack/hole or even audibly (high pitched whistle). Such events are almost always attributable to inadequate irrigation of the bed or to a fractured pipe. Ideally, daily subjective assessments should be carried out at the plant boundary to check on the levels of odorous emissions. Daily assessments can easily be done by the use of sniff tests or possibly detection tubes. A vigorous growth of foliage is to be expected on the surface of the bed. This is good in so far as it helps to remove nitrates and phosphates from the soil which would otherwise end up in the run-off water. The level of growth should be such that it is still possible to inspect the bed; if not the foliage needs to be cut. When cutting the foliage care must be taken not to damage the pipes underneath.

**Problems with soil based bio-filters**

- Bio-filters are large in size. Sizes can vary between 1, 500 to 7, 500m$^2$.
- The bed may become blocked by compaction. By annually turning the soil over, compaction can be minimised.
- The bed may crack because of insufficient wetting. If cracks do occur, non uniform flow of odorous air through the bed will occur - the air will preferentially flow through the cracks to atmosphere, thus reducing residence time and odour removal efficiency.
- Distribution pipes may flood because of inadequate drainage or an increase in the level of the water table.
- Distribution pipes may become blocked because of the presence of fine particles.
- This will result in uneven air distribution throughout the bio filter.

- There can be reduced efficiency at lower pH Yang and Allen 1994 reported that the biodegradation of Hydrogen Sulphide was strongly decreased at pH values of 3 and lower. However routine washing of the filter mitigated this efficiency.

**Plate 2.1 A BBK-bio filter at a Norwegian composting facility (building with flat roof in the foreground to the right) (Source: www.bbk.dk.)**

### 2.4.5.2 Non-soil bio-filters

A non-soil bio filter consists of a moist layer of material (typically peat, heather, compost, seaweed, or wood bark etc.), supporting a diverse microbial population together with a distribution system for supplying the contaminated air to the filter uniformly. The gaseous effluent is fed to the bio filter and the microbial population oxidises the undesirable compounds in the air stream to less noxious substances which then exhaust to atmosphere. Many different types of media exist for non-soil bio-filters; these include:

- Woodchip;
- Peat plus a ‘stiffener material’ (e.g. heather, polystyrene)
- Composted domestic waste
- Calcified seaweed

Whatever media is used, it has to give the following benefits:

- provide a damp environment for microbial activity Van Langenhove (1996)
- provide a damp enough environment to absorb all odour
- provide trace nutrients

Peat and heather bio filters have been used in a wide variety of applications and are broadly suited to odour problems involving large volumes of air at low to medium odour concentrations. Typically the life time of a bio-filter, if maintained correctly, varies from three to five years. Applications include:

- rendering plants;
- fine chemical and food/drink processes;
- waste water treatment works

Daily visual inspection of the bio-filter should be carried out to check for dry spots and/or channelling of irrigation water and/or the gas. Subjective olfactometry should be performed at least twice per day by a person who has not being exposed to the inlet odour. Tests done at a roof stack (possible if the bio-filter is roofed) are more accurate than those done on an open bio - filter.

Nozzles on the irrigation system should be inspected for blocking and periodic checks should be made on the volume of water being applied. As a rule of thumb, the irrigation rate should be 10 litres/m$^2$ of bed/day. All Bio - reactor systems are sensitive to changes in temperature and humidity and can change from design to design (Serageldin, 2001).

The pressure drop across the non-soil bio filter should be measured. Typically the pressure drop should be in the region of 35-60mm water however, if the pressure drop is approximately 100mm the bed has compacted and needs changing. It is good practice to turn over the bed of a non-soil bio filter at least once a year.

### Problems with non-soil based bio-filters

- To work effectively the microbiological population must be kept viable; this entails maintaining water content, pH, nutrient level and temperature within a relatively stable envelope.
- The monitoring of several parameters does add to the capital cost of the unit, however this is balanced by an increase in bed lifespan.
- The adaptation period of micro-organisms is long in comparison to the fluctuations in many industrial processes and hence bio-filters are best suited to processes with an output stream which changes sufficiently slowly to allow the microbial population to adapt.
- . Bio-filters can only be effectively used for continuous gas flow processes and not for batch processes - the microbial population would starve between each batch of gas.]
- For optimum odour removal efficiency it is essential to keep the bed irrigated. Non-soil based bio filters will cease to function if they are allowed to dry out and they are very difficult to rewet.
- Conversely, over watering should also be avoided otherwise the necessary microbes will be washed out of the bed. Typically, peat and heather bio-filters require approximately 60% moisture content to work well.

### 2.4.6 Bio-scrubbers

In a bio-scrubber, odorous gases are oxidised by microbe enzymatic activity to produce non odorous products. The contaminated gas is passed up a tower against a flow of water (counter current flow) containing a population of microbes suitable for oxidising the odorous components of the gas. The tower is designed to contain packing material on which the microbes adhere to form a biological “mat”.

These systems can be carefully selected to include a high proportion of Bacteria that utilises Hydrogen sulphide as their energy source. Some claim that they are up to 99% efficient but others argue that there is insufficient data following a review of the activated sludge in Bio-scrubbers by (Joanne E Burgess *et al.*2001). Bio-scrubbers are more energy intensive than bio filters since both water and air are being re circulated. However, their

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footprint is much smaller. The scrubbing tower should be designed to provide a contact time of about 1 second, but this will depend upon the composition of the inlet gas.

In theory, a bio-scrubber can be used whenever bio-oxidation is an appropriate solution to the problem and the solubility of the odorous target species is high. When compared to bio-filters a bio-scrubber has the advantage of requiring less land area and of discharging gas at height rather than at ground level. However, the technique has found little favour in the UK although it is widely used in continental Europe for agricultural and chemical applications. The main reason for its poor uptake in the UK has been because of poor design and operational knowledge. The first plants were poorly specified and instead of being used to treat low flow rate, very soluble and biodegradable gases they were used for high flow rates, low solubility and low biodegradability gases. Consequently the plants failed and had to be replaced

This is typically undertaken by chemical analysis or odour assessment of the inlet and outlet gases, e.g. pH, biological oxygen demand (BOD) etc. They can adapt to changing odour composition by changing both the number and the microbes present. The system is very well suited to sewage treatment and running costs are lower than some other systems. Bio-scrubbers can be > 99% efficient and do not need to replace media.

### 2.4.6.1 Problems with Bio-scrubbers

- Biomass may build up within the tower blocking the circulating water. Easy access to remove biomass is required.
- Sometimes there can be an odour emitted form the liquid circulation hold-up tanks. If chemicals are used to remove the odour care must be taken to ensure that they do not poison the microbes within the tower.
- Microbes can be 'carried over'. The air stream can carry the microbes to the exhaust.
- Therefore microbial activity needs to be continuously measured and occasionally additional microbes will need to be added to the tower.

### 2.4.7 Trickle-Bed filters

Trickle-bed filters are a hybrid of bio-filters and bio-scrubbers. Contaminated gas passes through a packed bed which supports an active microbial film. The support material may be either a traditional material (e.g. heather) or an inert substance. Water from a sump is sprayed on top of the bed and is continuously re-circulated. The gas flow being treated may be either counter current or cocurrent. Bio systems can oxidise single pollutants or mixtures of pollutants in an air stream.

### 2.4.8 Absorption

Absorption is defined as a process which involves mass transfer between a soluble gas and a liquid solvent in a gas-liquid contacting device. Vapours and gases are absorbed from a contaminated exhaust stream into a chemical solution. The liquid phase is generally recirculated with a small amount being continually being bled off and the same amount of fresh reagent being introduced. The main requirement is that the contaminated air should be brought into contact with the liquid. Special packing materials may be used to increase the gas-liquid contacting area.

Gas absorbers which use water as the scrubbing liquor commonly have odour removal efficiencies of 90%. To increase absorber efficiency, chemicals are added to the scrubbing water to remove specific odorous compounds. The odorous components of a gas stream are transferred to the liquid phase where a chemical reaction takes place. Typically acidic or alkaline gases are absorbed into pH controlled solutions, whilst other odours are absorbed into appropriate chemical solutions according to composition.

The use of various forms of packing or other types of gas-liquid contactors will improve odour removal efficiency but at the expense of increasing pressure drop The use of chemical reagents carries its own problems. If process conditions vary outside of control limits, droplet carry-over can occur. The use of oxidants can sometimes lead to the formation of other odorous compounds within the tower and poor effluent management can create odour sources. Therefore the absorber, if poorly designed and controlled, can become a secondary source of odour. It should be possible to design a system to maintain a residual post-treatment odour emission of below 1,000 ou/m$^3$ Absorption is good for removing odorants of known composition and may also be used as an after treatment to incineration, if acid gases are produced. Gas temperatures of up to 70°C can be tolerated,

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but at more elevated temperatures, product solubility may change, particulate production may occur and downstream condensation may become a problem.

The technique has been used with varying degrees of success for a number of different types of odorous emission. These include the emissions from rendering plants, tanning, vegetable hydrolysis, tobacco processing, pharmaceutical production, waste water works.

There are four factors which determine the most appropriate type of adsorber to be used:

- required abatement efficiency
- energy efficiency
- reagent requirements
- properties of the incoming gas stream.

Absorption systems can have either aqueous or non aqueous liquid phases. The selection of the relevant absorbing media will depend upon the properties of the odorous compounds.

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**Solubility characteristics of common odorant species**

***Water is suitable for absorbing soluble acidic gases such as***

:Hydrogen chloride

Hydrogen fluoride
Silicon hexafluoride
Ammonia

***Alkaline solutions are suitable of absorbing less soluble acidic gases such as:***

Sulphur dioxide
Hydrogen sulphide
Chlorine
Very soluble acidic gases to very low levels

***Acid solutions may be needed for the absorption of:***

Very soluble basic gases to very low levels
Amines

***Oxidizing solutions can be used for:***

Oxidation of by-products of the above reactions
Control of some soluble organic odours

Some commonly used oxidizing agents are:

- Permanganate
- Hypochlorite
- Chlorine dioxide
- Ozone
- Hydrogen peroxide
- Bisulphite.

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The driving force for odour removal by absorption is the difference between the partial pressure of the soluble gas in the gas mixture and the vapour pressure of the solute gas in the liquid film in contact with the gas. Mass transfer occurs by molecular diffusion across the gas/liquid interface. Gas absorption is a rate process and consequently the concentration gradient (reaction driving force) and the surface area of contact between the liquid and gaseous phases are crucial design parameters.

### **2.4.8.1** Spray tower

Liquid enters the top of the tower via spray nozzles and the dirty gas stream passes up the tower. Pre-formed spray scrubbers can be designed such that the gas flow is vertical or horizontal, counter current, concurrent or cross current. Liquid droplets produced by the spray nozzles fall down the tower through a rising stream of dirty gas. Gas/liquid contact at the droplet surface enables mass transfer to occur.

Spray towers can be used for trace gas removal and particle collection. The technology has been successfully used by various sectors of the chemical industry for absorbing acid gases and odours, for ammonia hydrolysis and for particle abatement.

Problems with this technology

- The plugging of the spray nozzles.
- High removal efficiencies cannot be achieved.

### **2.4.8.2** Plate Absorbers

Plate absorbers consist of a vertical tower with several horizontal perforated trays (sieve plates) stacked inside. Baffles are situated a short distance above the apertures in the plates. Liquid enters the top of the tower and flows along each of the trays successively. Dirty gas enters the bottom of the tower and flows upwards, passing through the perforations in the plates. The velocity of the gas is sufficient to prevent liquid seepage through the perforations. Absorption efficiency can be increased by adding more plates to the absorber (increasing tower height) and by increasing liquid flow rate. Plate absorbers can operate at higher liquid flow rates than packed towers and are able to tolerate fluctuations in gas flow and temperature. Absorption efficiency increases as pressure drop across a plate increases. Low outlet emissions can be achieved as the final gas liquid interface is between fresh liquid and comparatively clean gas. Plate absorbers are effective for trace gas removal and particle collection. The technology has been successfully used in the chemical industry and industrial heating plant for the absorption of acids (in water), $SO^2$ (using sodium sulphite) and odour.

**Problems with Plate Absorbers**

- Scaling can be a problem with plate absorbers and hence they are not suitable for use with slurries, e.g. lime.
- Plate absorbers are not suitable for use with foaming liquid

### **2.4.8.3** Packed Bed Absorbers

Packed bed adsorbers are the mostly commonly used in the treatment of odour. They consist of an outer shell containing a bed of packing material on support grids, liquid distributors, gas and liquid inlets and outlets and a mist eliminator. The absorbers are designed so that liquid is distributed continuously over the packing material forming a film which provides large surface areas for gas/liquid contact. The contaminated gas flow through the packed bed can be either counter current (gas flows in opposite direction to liquid flow), con-current (gas and liquid flow in the same direction) or cross current (gas and liquid flows are perpendicular). For the treatment of Hydrogen Sulphide alkaline is considered the most efficient absorption type scrubbing (Weast ,1976).There are various types of packing material which can be packed in random or in a regular arrangement. The most common types are

- raschig rings
- lessing rings
- pall rings and modified pall rings - most commonly used in industry
- berl saddles
- interlox saddles
- tellerettes

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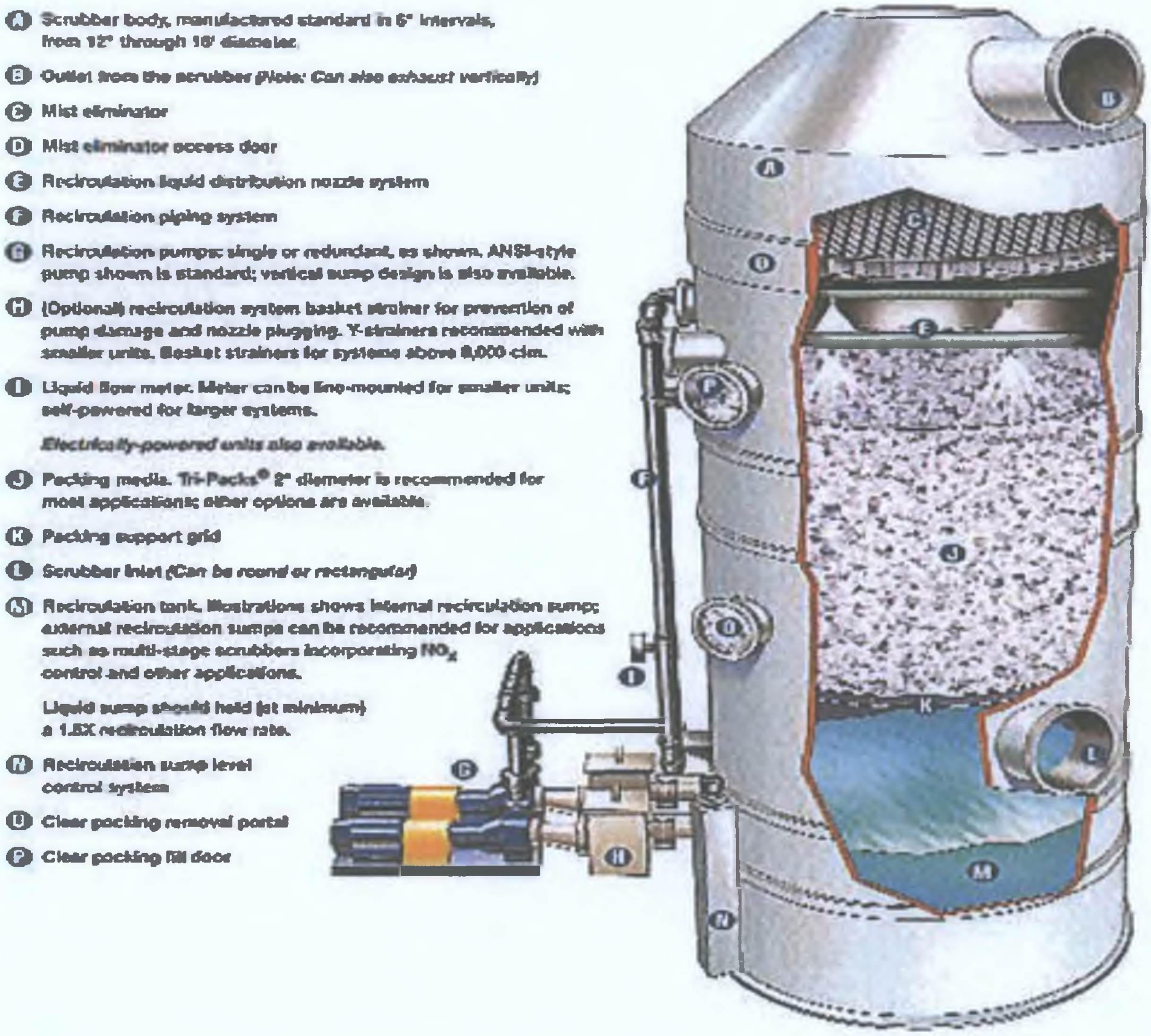

**Figure 2.3. Packed Bed Absorber (source www.epa.gov)**

Packed bed absorbers, with the appropriate reagents, have been successfully used for absorbing gases and odours from boiler flue gases, chemical, food, water treatment and petroleum process. Packed bed absorbers are not suitable for treating gases containing high concentrations of particles - particles cause plugging of the packed bed. In some processes it may be necessary to install a separate particulate abatement device upstream of the packed bed absorber.

### 2.4.8.4 Hydrogen Peroxide Scrubbing

The use of hydrogen peroxide as an alternative oxidant to the more commonly used sodium hypochlorite is finding increasing use for a number of reasons, including:

1. It has become much more cost competitive in recent times and best suitedto warmer climates, ( Tomar, 1994)

2. It is available in much higher strength solutions than hypochlorite which means for a given application the volumes to be transported are less, storage tanks can be smaller and dosing pumps and piping systems smaller. These factors also help improve the cost competitiveness of peroxide. This can be especially so for remote locations where transport costs can be very significant.

3. No residual chlorine or chlorinated by-products are produced in either the gas stream or the liquid effluent ex the scrubbing system. This is sometimes perceived to be a benefit and is sometimes a real benefit.

There are now a number of reports in the literature of odour control systems which have either been designed from the start to use peroxide or have been converted from hypochlorite to peroxide with apparent significant success. At this stage two apparent issues yet to be resolved with peroxide however:

The concentration of hypochlorite in the scrubbing liquid is usually measured using oxidation reduction potential (ORP) with the makeup of fresh hypochlorite solution being controlled to maintain a fixed ORP. There are conflicting reports on the ability of ORP as a control variable for peroxide. It is apparent that using ORP for peroxide control is more difficult than for hypochlorite and whether it is really a viable long term method is yet to be established. This has led at least one instrument supplier to develop an instrument specifically designed to control peroxide concentration in scrubbing solutions of this type.

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Its ability to effectively scrub a variety of VOC and compounds other than hydrogen sulphide. There is no doubt that it is effective on hydrogen sulphide as has been proven in applications in for example waste water treatment plants. What is not yet known is how effective it will be on a lot of other odour sources where other odorous compounds are more dominant. The reports are encouraging but more experience needs to be generated to be certain.

### **2.4.9** Lagoons

Two systems used to improve lagoon effluent systems are the "Sutton" and the "New Hamburg" processes.

The "Sutton" concept consists of Nitrifying extended aeration plant followed by polishing lagoons. These plants produce an improved effluent quality relative to conventional facultative lagoons in terms of BOD and the TSS. concentrations. Cleaning out of the lagoons is required every 5 – 7 years.

The "New Hamburg" process resulted in significant improvement in effluent quality in terms of BOD, TSS. Ammonia and Hydrogen sulphide concentrations. Disadvantages of both processes are that they are both very expensive (Melcer, 1995).

Photosynthetic Bacteria for Hydrogen Sulphide removal from anaerobic waste treatment plants was investigated by growing fixed films of photosynthetic bacteria in a fixed column. Results showed that Hydrogen Sulphide removal efficiency of 81 – 95% during a 24 hour retention time.The green photosynthetic sulphide – oxidizing bacterium "Chlorobium" was identified as a common organism in this phototube. There is no need for aeration or chemical addition and further research into process design is necessary before full scale application of the technique is possible (Kobajashi, 2003)

### **2.4.10** Thermal Incineration

Thermal incineration has been used successfully in many industrial application e,g, animal rendering, waste - water treatment, resin and printing works. It has the advantage of being applicable as a method of odour control because all odours can be oxidised at high temperatures, whereas the application of other methods is more restricted.

#### **2.4.10.1** Recuperative

Recuperative incinerator systems use heat exchangers to preheat the waste-gas stream prior to combustion, and may recover heat to generate steam or hot water or to provide process heating. Shell-and-tube and plate-heat exchangers may be used. Shell-and-tube units are more common and have advantages when temperatures exceed 540°C. Effluent gas stream from the incinerator is used to pre-heat the incoming gas stream, thus reducing the amount of energy required to heat gases in the incinerator. This type of system is particularly suitable for gas streams of comparatively low flow rate and high levels of odour. 50-80% heat recovery is generally achieved (US EPA, 2001).

Recuperative incinerators have similar destruction efficiencies to thermal incinerators, but they can be limited by the need to operate the heat exchanger at lower temperatures to prevent damage. These incinerators are usually more economical to operate than straight thermal incinerators because they can recover 40 - 70% of the waste heat from the exhaust gases, but they do have higher maintenance costs. Time, temperature and turbulance are considered the most important factors in the design paramaters (ICAC 1999).

#### 2.4.10.2 Regenerative

Effluent gas from the incinerator passes through several ceramic bed heat exchangers. They are used to pre-heat the incoming gases, thus reducing the amount of energy required to heat the gases in the incinerator in order to burn off the odours. Oxidation of the gas also continues in the ceramic beds. The system is operated so that the beds alternate between, heating, cooling and purging. This type of system is particularly suitable for gas streams of comparatively high flow rate (up to $40m^3/s$) containing low levels of odours; 80-95% heat recovery is generally achieved. Contaminant destruction efficiencies of thermal regenerative incinerators typically range from 95 to 99%, while catalytic units range from 90 to 99%. Catalytic units have the advantage of being able to remove carbon monoxide from odour - laden air.

There is also the potential for secondary heat recovery, e.g. to obtain hot water, space heating etc. using both systems.

Regenerative incinerators are expensive and difficult to install, are large and heavy, and have a high maintenance demand for moving parts. Advantages include their low fuel requirements, an ability to operate at higher temperatures than recuperative incinerators, and they are suitability for high-flow, low-concentration waste streams.

Incineration has the advantage of being almost universally applicable as a method of odour control because all organic odours can be oxidised at high temperature, whereas the application of other methods is more restricted EPA (1995) . Temperatures can be brought to 1000°C if necessary depending on the type of destruction required.(Gay 1997)

**Problems with thermal incinerators**

- High capital and operating costs when compared to other forms of odour abatement.
- Any compound containing sulphur or chlorine atoms which pass through the incinerator will generate $SO_2$ or $HCl/Cl_2$ acid emissions respectively and further treatment of the exhaust gas may be required.
- Burners need to be inspected regularly to ensure that there are no deposit formations.
- If deposits are a problem then effective pre-treatment may be necessary to clean the contaminated air before it enters the burner.
- Incinerator malfunction can arise from a variety of causes and sooty emissions and odour can result if effective plant maintenance is not undertaken.
- Mechanical breakdown can be a significant problem; commonly it is the fans that fail.
- Failure often caused by dust abrasion, so the fan should be fitted downstream of dust removal equipment.

### 2.4.10.3 Kilns and Boilers.

These can be used to incinerate odours where the temperatures and residence times are in the appropriate range. This becomes an attractive choice if a kiln/boiler is already on site and particularly so if the boiler can be incorporated into the design stage. It must be remembered that not all boilers or kilns work for 24hrs/day, and hence they may not be able to treat the odour all the time. There are a number of rendering plants in the UK that use their steam raising boilers as their primary form of combustion to treat process gas emissions. The technique has the ability to destroy the typical rendering plant odour, but may replace it with a typical boiler stack emission odour. The disadvantages of this approach are that a secondary combustion unit may need to be on-stand-by in case the main boiler fails. Combined heat and power plants have been used to treat odour emissions arising from starch production and they have also been used to treat the high sulphide content of mineral oil absorber emissions arising from rape seed oil extraction.

### **2.4.10.4** Catalytic incineration

Catalytic incineration is similar to thermal incineration but the main difference is that the oxidation reaction takes place on the surface of the catalyst rather than in free air. The use of a catalyst allows the same degree of combustion completeness to be achieved at lower operating temperatures and hence lower fuel consumption. Catalytic incineration can take place at temperatures of 300°C to 450$^0$C and a gas residence time of 0.5.-1.0 second (Paillard and Blondeau, 1988). Another advantage of catalytic when compared to thermal incineration is that its footprint is smaller.

The basic principle of operation is that the dirty gas stream enters the unit and is pre-heated in a heat exchanger. A burner heats the stream and it then proceeds to the catalyst section. In the catalyst section odorous contaminants and oxygen diffuse from the air stream and are adsorbed onto the catalyst surface. Oxidation takes place and the products are desorbed into the air stream. The catalytic reaction is temperature dependent and for efficient incinerator operation the temperature is typically between 350 - 400$^0$C. The exhaust gas is then passed through a heat exchanger which is used to pre-heat the incoming air stream.

There is potential for secondary heat recovery, for example to obtain hot water, space heating etc. Catalytic incineration is an appropriate odour abatement technique when the concentration of odorants is high and there is little or no particulate matter. Abatement efficiencies of >90% are normally achieved. Catalyst companies propose different catalyst formations for cobustion of different contaminants (Berndt and Landri,2002). This may be a limit to increasing the flexibilty of this technology.

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**Problems with catalytic incinerators**

- Secondary waste generation - spent catalyst
- Flame failure can occur if there is a sudden surge of air through the system. To counter this pressure releases should take place slowly and an audible flame failure alarm should be installed.
- Mechanical breakdown can be a significant problem. Fan breakdown is the most common failure and it often caused by dust abrasion (fans should be fitted with dust removal equipment).
- All catalysts used are prone to spoiling by poisoning agents (chemicals which chemically combine to the active catalyst material), fouling agents (contaminants which coat the surface thus interfering with the adsorption/desorption process), activity suppressants (reversible masking agents) and blinding (coating by dust). Pre-treatment of the inlet air stream is very important.
- The cost of pre-treatment and spent catalyst may make catalytic incineration similar in costs to thermal incineration.

#### **2.5.10.5** Flares

Flares are primarily safety devices, which deal with flows of short duration such as an upset condition or an accidental release from a process, rather than a control device that treats a continuous waste stream.

Flares are generally categorised by the:

- Height of the flare tip - ground or elevated
- Method of enhancing mixing at the flare tip - steam-assisted, air-assisted, pressure-assisted or non-assisted
- Candle type or enclosed flare.

Elevating the flare can prevent potentially dangerous conditions at ground level, and also allows the products of combustion to be dispersed. Flares can be used to control almost any odour stream, and can typically handle large fluctuations in concentration, flow rate, and other characteristics. The primary application of flares is in the petroleum and petrochemical industries, but flares are also common for landfill gas treatment, and biogas from anaerobic digestion of sludge at wastewater treatment plants. Pilot flames can run continuously or by auto-ignition. It is important to monitor the flare to ensure that the flame does not go out in strong winds. Monitoring may be by regular inspection or automatic monitoring and an alarm.

### **2.4.11** Low cost odour abatement methods

There are some methods which could be considered in the low cost bracket which industries and plants could implement initially before major capital expendiure.

#### **2.4.11.1** Odour modification

The term odour modification relates to the discharge of additional volatile substances into the atmosphere in order to change the perceived character or perceived intensity of an odour.

Other terms which have been used to describe this technique are:

- Odour masking - which refers to a change in odour quality in order to make the original odour more acceptable and/or unrecognisable by the addition of a more pleasant odour. The application of agents can become dangerous if they mask the odour of high and toxic concentrations of VSCs. Also when dilution of the masking agent to below its threshold value occurs before the malodorous compounds have reached their odour threshold value odour problems can arise at a certain from the source (Anderson, 1980)
- Odour counteractant - describes the phenomenon whereby a mixture of mal-odorant and counteractant may smell less intense than the sum of the intensities of the unmixed components or the mal-odorant alone.
- Neutralisation - refers to the effect where the interaction between the chemical receptors in the nose and the odorous molecules are modified in some way so as to modify the human response.

Both odour masking and odour counteraction can be used. An unpleasant odour can be masked by the addition of another stronger odour and if the stronger odour is pleasant, then the result might be acceptable for a short time. The application of odour counteractants to a 'real' odour is problematic, as they may contain odorants whose concentration may change over time. These variables make it difficult to ensure that unpleasant odours are 'blotted out' at all emission levels.

The application of odour modifiers can be:

- Direct addition to the odorous material at source. Here the modifier must be able to withstand the same conditions as the material being processed.
- Discharge to atmosphere at a distance from the source, between the source and the community, by atomisation and spraying.

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The advantages of odour modification methods are:

- Modest capital outlay;
- Atomiser units are portable, can be rapidly deployed;
- Highly visible means of being seen to take action over a problem.

The on-going cost of the modifier agent can be very expensive and maintenance costs can be high as fine spray nozzles can be prone to blockage. Examples of the use of products described as counteractants have been used around the tipping faces of landfill sites; the effectiveness of their use has been questioned. In light of the general reasons given above the application of modifier agents is severely restricted. Many local authorities' guidance notes forbid the use of odour counteractants and the EPA in recent guidance has stated their disapproval of such systems except under defined circumstances.

Possible field of application for these products are:

- As a temporary control measure whilst the details of an active abatement system is being considered.
- The odour problem is short term and it is not BAT to take other action.

#### **2.4.11.2** Landscaping (i.e. tree planting and earth banking)

Trees are only effective in minimising the impact of odour if they are densely planted, close to the odour source, taller than the odour source emission point(s), the receptor sites are close to the odour source and trees, and if the weather conditions are stable. If these four criteria are met, the trees will promote turbulence which will result in greater dispersion of the odour and hence, minimise the impact on the local area.

Earth banking has also been used to minimise odour impact but for it to be effective, the same criteria must be applied as for tree planting, e.g. it must be close to the source, taller than the odour source emission point(s) etc.

### 2.4.11.3 Condensation

If an odorous gas stream contains high concentrations of vapour then condensation can be used to reduce odour. There are various methods for bringing about condensation,

- Direct contact condensers - a cooling liquid (at ambient temperature or slightly below) is sprayed into the vapour-laden gas flow. This is the cheapest and simplest method.
- Indirect contact (surface) condensers - these are cooled with water or a cooling liquid.
- Coolant usually circulates in the tubes and vapour condenses on the outer surfaces and drips into a storage tank.
- Air cooled surface condensers - air cooled finned tubes are used to cool down the vapour sufficiently for condensation to occur.
- Pressurised condensers - gas is compressed before cooling. This is the most efficient condensation method but also the most expensive.

The problems arising with condensation are that energy inputs are high, they condense everything (odorous and non-odorous compounds alike) and they are expensive.

The process of condensation is mainly used as a pre-treatment to other odour abatement technologies. The use of condensation is a key element with the treatment of discharges from any cooking operation and is used throughout the rendering industry.

### 2.4.11.4 Catalytic iron filters

Catalytic iron filters remove hydrogen sulphide from odorous air streams in the range of approximately 10 to 500ppm and achieve removal efficiencies of 60 to 95%.

At present, catalytic iron filters are primarily used by the water industry where high levels of hydrogen sulphide can be found. Other applications include anaerobic processes in the food industry. Typically a catalytic iron filter is fitted prior to a bio-filter or an adsorption unit to minimise peak loads and average out inlet concentrations.

A catalytic iron filter comprises a cylindrical steel vessel with perforated retaining plates at the inlet and outlet and a fixed bed of rusting mild steel packing elements in between.

Odorous air passes through the bed where hydrogen sulphide, which is the prime constituent, reacts. For this system to be effective the inlet air stream needs to be reasonably moist with a relative humidity of greater than 75%. The surface of the packing elements provide sites for the catalytic oxidation of hydrogen sulphide by iron oxide ($Fe_2O_3$) covering the packing. The reaction requires water to be present and produces an intermediate compound, iron sulphide ($Fe_2S_3$) before immediately regenerating the $Fe_2O_3$ from atmospheric oxygen. The intermediate $Fe_2S_3$ is oxidised to elemental sulphur which gradually forms a film on the packing surface. After a period of time the film formed by the sulphur blocks the air spaces between the packing necessitating packing replacement. Another by-product is sulphuric acid which can be removed as an intermediate trickle of dilute solution to a suitable drain. It must be remembered that a catalytic iron filter is not an odour control technique in itself; it protects and improves the cost effectiveness of the polishing unit (e.g. a bio-filter or scrubber).

### **2.4.12** In stack abatement techniques

The principal techniques used for "in stack" odour control, are:

- ozone;
- ultraviolet.

These techniques work by either injecting ozone directly in the odorous gas stream or injecting UV excited radicals into the gas stream. The injected elements oxidise some of the odorous compounds in the gas stream. Along with odour reduction there has also been reduction in colour ,turbidity, COD and BOD when used in tertiary treatment plants (Balakrishnan,2002). Although ozone is a powerful oxidising agent, for complete gas phase reaction considerable residence times are required. The rate of oxidation varies from compound to compound and in addition the rate of oxidation is highly dependent on temperature. With this type of technique considerable care must be taken to control the ozone dosage to ensure that under conditions of fluctuating odour levels, a high, and potentially dangerous residue of un reacted ozone is not discharged. In general, it is impracticable to build reaction chambers with sufficiently long residence times to ensure complete oxidation of all compounds, thus its application is limited to highly reducing compounds, e.g. Hydrogren Sulphide. Some of the water companies have adopted this technique and it has also been piloted by the food flavouring industry. The principles of UV to abate odour are similar to those for ozone. It is currently being applied to the animal feed industry.

The drawbacks of both techniques are:

- High operating cost.
- Potential safety implications.
- Pre treatment is required to minimise particulate fouling.

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## 2.5 Case Studies of Biological Treatment Systems

Case studies were reviewed in order to assist with the decision regarding the type of trial for Aughinish Alumina waste effluent plant.

### 2.5.1 A WWTP in Adirida, Kuwait

The wastewater treatment plant concerned is a very large plant located in Adirida, Kuwait. Over the last thirty years Kuwait city has undergone unusual population growth which has reflected the need to expand their waste water treatment plant. The original plant was constructed in 1965, with a capacity of 100,000m$^3$/day and came into service in 1970 and was extended in 1984 to a 150,000 m$^3$/day capacity. In the meantime the plant has struggled to handle the increased loading due to the ongoing population increase. The plant and the numerous pumping stations have been the source of continuous public complaint. The main cause of odours has been Hydrogen Sulphide generated within the wastewater collection systems and partially released at the various processes within the treatment plants. Measurement of sulphide concentrations in the raw water ranged between 10mg/l and 47mg/l and based on a 150,000 m$^3$/day flow and the sulphide content averaged around 5000kg/day. The seriousness of the problem can be gauged by the fact that 1% release of this sulphide would result in a 10 ppm concentration of Hydrogen Sulphide in the atmosphere throughout the plant.

#### 2.5.1.1 Odorous gas formation

- The high content of sulphate in the wastewater is due mainly to the original sulphate content in the water supply.
- The low per capita water consumption and consequently the high concentration of organic material in the waste water. This results in wastewater that becomes septic or anaerobic in a very short period and in turn leads to odorous gases.
- The flatness of the terrain and the low velocities in the collection systems leads to grit and organic deposits in the water collection system.
- The long retention times in the collection system due to low gravity and the length of lines.
- High prevailing temperatures.

#### **2.5.1.2** The treatment process

The Inlet Works comprises of collection tanks, screening, grit removal, ph adjustment, flow equalisation basins and air injection. Adjacent to the inlet section is an odour control facility and includes the following.Four stage scrubber units.

- One exhaust fan and ducting.
- NaOH, HCl and activated Carbon dosing system for the scrubbers.
- Alkali and acid pumps.
- One air compressor and injection piping
- NaOH dosing pumps.

First stage aeration and settling consists of an activated sludge process designed for the removal of carbonaceous organic matter, this system is reportedly overloaded and efficiency below desired limits, this in turn is overloading the downstream processes. The mechanical aerators cause turbulence and result in excessive and uncontrolled stripping of odorous gases.

Second stage aeration and settling is designed to remove the balance of the organic carbonaceous matter and to oxidise the nitrogenous matter. Due to the reduced efficiency of the first stage nitrification of the effluent is not being achieved and in this tends to increase the chlorine requirements and reduce the effectiveness of the disinfection process .An advanced treatment stage consists of chlorination, contact tanks, rapid sand filters, and discharging to the effluent utilities.

Sludge treatment consists of pre- thickeners, digesters, gas recovery steam heating; heat-exchangers gas holders, filter presses, and drying beds.

The treatment of the effluent should be such to achieve the following;

- Suspended solids concentration below 10mg/l
- BOD below 10mg/l
- Ammonia below 3mg/l
- MPN below 2.3/100ml
- Nitrates, phosphates and potassium do not have any limits in view of their nutrient value in agriculture.

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The odour control at the inlet section worked reasonably well but the excessive stripping of odorous gases down stream of these facilities were deemed unsatisfactory and further controls were required and options available are outlined below.

- Look at a more radical solution.
- Ph adjustment at the inlet is not a cost effective method.
- The treatment of sulphides in the gaseous is not cost effective due to the low efficiency of this process
- Biological and chemical oxidation of sulphides in the solution form was considered the most effected method to deal with the high sulphides in the Ardiyah plant.

#### 2.5.1.3 Odour Treatment Programme

It was decided that biological oxidation of the sulphide using specific chemo-autotrophs would minimise sulphide stripped out in the aeration process. The aeration system was stripping the sulphide and thereby creating odour problems. It was decided to trial a product called Bio-Treat OC and in trials it was successful in reducing the sulphide concentration. By placing a number of Bio-Treat Units around the Plant area, large volumes of concentrated bacteria are cultured where and when required. At the start of each 24-hour growth cycle 100 millilitres inoculum and 1 litre of nutrient is added up to 200 litres of clean freshwater. After 24 hours in a temperature-controlled environment and with continuous aeration, the bacterial population grows up to a concentration of bacteria $10^{10}$.

Every day the bacterial inoculum was grown up and added to the primary treatment tanks. This bacteria greatly reduces the odours produced by the plant and additionally reduces the BOD, and sludge volume. From the graph below the reduction can be seen over the nineteen day period from 800mg/l to zero.

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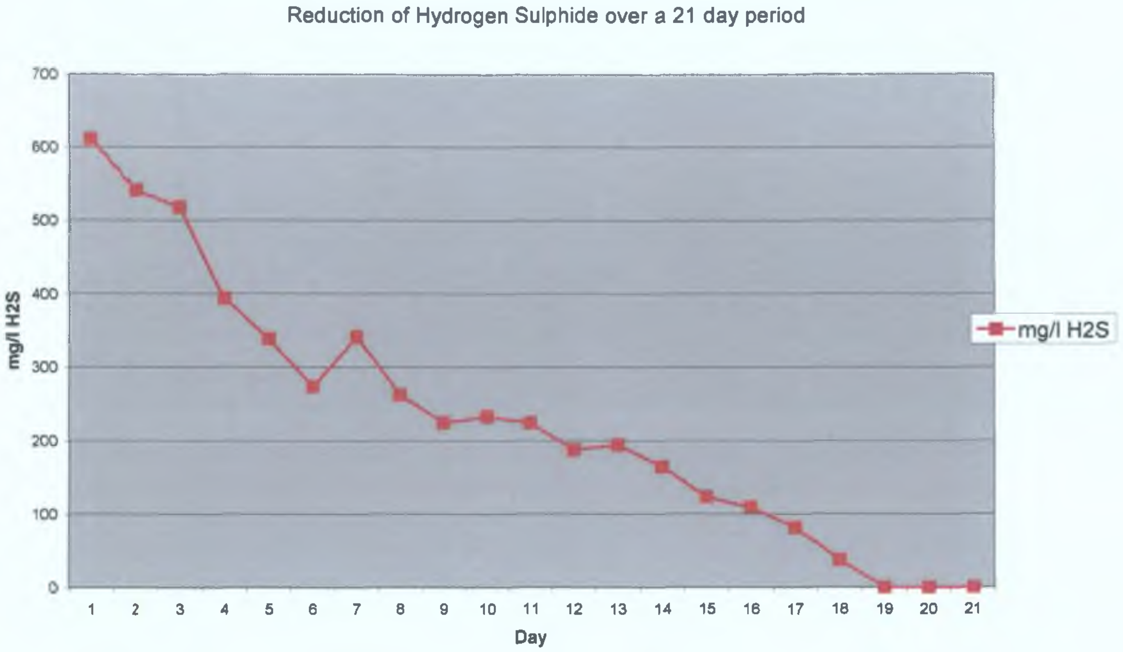


**Graph 2.1: Reduction of Hydrogen sulphide concentration using Bio Treat OC at a wastewater treatment plant, Adirida, Kuwait, (Source Bio-industries ltd.).**

Following the trial there was a definite improvement in the biological digestion of the organic waste being received by the plant. The effluent being received by the plant was in a very septic state and the system improved treatability and the emissions of certain types of gases, particularly Hydrogen Sulphide. This was particularly evident in the first stage of treatment. There was consideration for improving the effluent discharge and also to improve sludge drying. The plant had problems drying their sludge due to the high levels of undigested organic matter and poor settling. Increased microbial additions and the scope of the bio-enhancement program further reduced the production of odours, improved the management characteristics of the sludge and reduced the amount of solids (fats and grease) building up and odours produced at the various pumping stations around the plant.

### 2.5.2 Odours from a lifting Station.

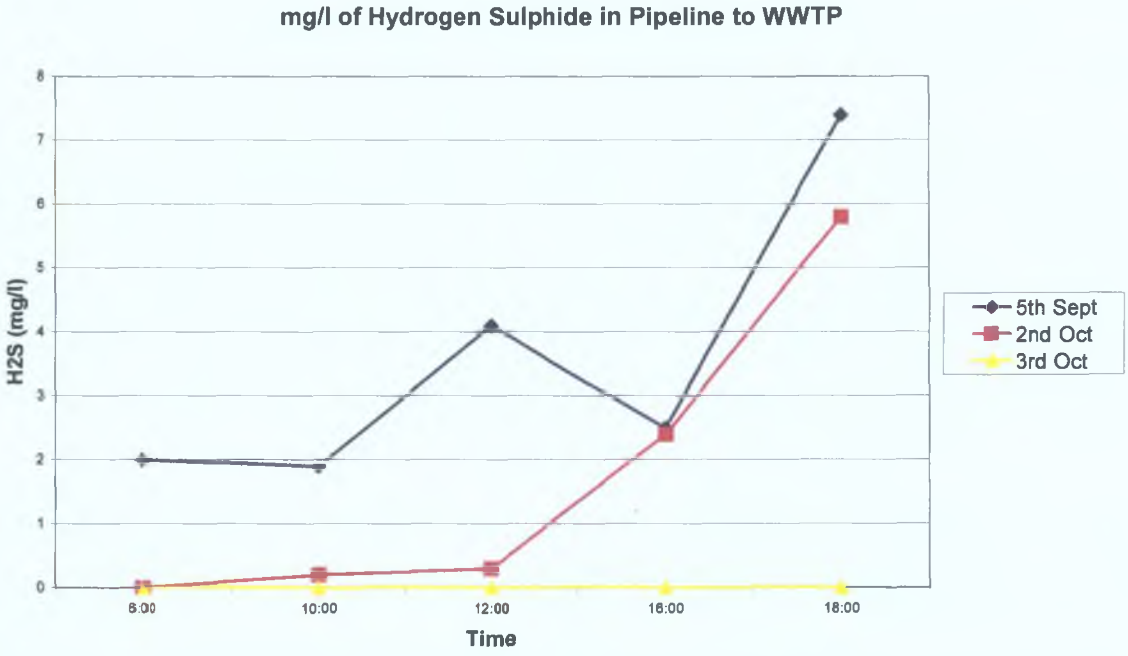
The pumping station is situated north of the town of Crosby in the UK. The station is the second of two stations pumping the domestic sewage to a treatment works in Bootle. Domestic sewage was at one time pumped into the Irish Sea. Changes in UK and EU legislation have meant that this practice is no longer acceptable and from 1997 all sewage of this nature will have to be treated to legislated standards. To pre-empt this change Sefton BC and North West Water installed a pipeline several kilometres long to collect and transfer the domestic waste from Crosby to a treatment works in Bootle. Unfortunately because of the nature of the waste in the pipeline anaerobic gases such as hydrogen sulphide caused severe odour problems to the local population.

#### 2.5.2.1 Initial Evaluation

Several schemes were considered by the local council and North West Water to try and overcome the nuisance; these included charcoal filters, sealing vents and chemical treatment processes. However, it was decided that a two month biological treatment trial should be initiated. In the initial stages a mixture of various micro-organisms were added to the system to seed the pipeline. Once these became established a collection of micro-organisms sold under the brand name of Bio-Treat OC were added on a daily basis. After one months treatment it was decided that the daily dosage of 200 litres should be staggered throughout the day to suit the peak flows during the day i.e. early am and evening time. It also allowed the micro-organism to start reverting to their facultative anaerobic state so that they were able to act more quickly when discharged to the wet well. A 1,000 litre tank was installed at the site for dosing to the system.

### 2.5.2.2 Trial Results

The predominant anaerobic gas which was of concern was Hydrogen sulphide. The level of the gas before treatment was 80mg/l. This was reduced as can be seen from the graph below.



**Graph 2.2 Showing hydrogen sulphide concentration in a sewage pipeline.**

Following the successful reduction in the levels of Hydrogen sulphide the decision has been taken to continue with the Bio-Treat System. An added bonus to the programme has been the reduction in the volume of sludge at the pumping station sump. Normally this level is between 0.5-0.7 m thick and has to be sucked out and taken from site by a contractor. At the last inspection there was only a thin film of sand silt in the bottom of the sump. areas. The reduction in cost of this extraction process more than covers the cost of the biological treatment programme.

## 2.6 Site Visits

### 2.6.1 Introduction

The decision to visit other sites was taken in order to gain further knowledge on wastewater treatment plants and find out how these plants controlled odour emissions.

### 2.6.2 Merck, Sharp & Dohme

The purpose of the visit to Merck, Sharpe &Domhe was to look at their effluent plant and gain some information on their system and find out how they handled any problems with Hydrogen Sulphide odours. They dose with ferric nitrate to control Hydrogen Sulphide odours in their effluent plant. .Merck Sharp and Dohme are a subsidiary of Merck, & Co Incorporated one of the largest healthcare companies in the world. They have been in Ballydine Co.Tipperary since 1976. The parent company has discovered many critically important healthcare products including those used in the treatment of high blood pressure, high cholesterol, angina ,and osteoporosis .Ballydine is an Organic Synthesis Plant where production is carried out in two phases, “wet” and “dry”. In the wet section, liquid and solid raw materials are mixed and processed. The final product is then refined and packaged in the dry phase.

#### 2.6.2.1 Ballydine WWTP Units (1/2)

The influent from the site averages 2,800m$^3$/day and all waste water streams from processing operations pass through a bar screen / solvent interceptor / wet well and then is pumped the equalization tanks (2 No.) These two tanks have a capacity of 2,500m$^3$ each. The next stage is neutralization and nutrient additions. The wastewater is neutralized in coarse and fine pH control in the range of pH of 6.5 -7.5. Primary clarification is the first stage of solids removal and the overflow system goes to the aeration system with one basin on-line and one off line.The mixed liquor tank mixes the influent and returned sludge prior to aeration. The mixed liquor biomass in the aeration basins degrade the BOD {solvents}to carbon dioxide and water. In the next stage of Secondary clarification polymer is added to the biomass to aid separation of the clean

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supernatant and the biomass. The effluent is re-aerated in the tertiary lagoon prior to discharge to the river. Capacity in the lagoon is 15,000m$^3$ and retention time of 5-8 days. MSD effluents are both organic and inorganic in nature Inorganic effluents such as chlorides (chloride salts / anhydrous HCl ) and sulphates (from the neutralization of caustic from the scrubber towers, and the use of salts in the DIW system ) .Organic effluents are treated biologically in the onsite WWTP.The inputs are 90-95% solvent based and 5-10% sewage.The addition of cdor block (ferric nitrate) helps to combats sulphides and corrosion. Immiscible solvents are used onsite include Toluene, Heptanes, Hexanes, MCB ,Ethyl Acetate and IPAC.

Problems with their use are listed below:

- LEL Elevations - E.Q. Tank Headspace
- Fugitive Emissions
- Mass Balance Closure
- Site Odors

### 2.6.2.2 Sludge Handling and Odour Control

Types of sludge for processing include the following:

- Primary Sludge
- Excess Activated Sludge

The rate of excess sludge production depends on the f/m ratio,extended aeration plant has a low f/m ratio (0.1 - 0.2) [f/m = BOD per day / Total Biomass].The under flow of the Primary clarifier is at 1% solids which are transferred to the aerobic digestion system with and the excess going to the mixed liquor tank. Across the digester and the gravity thickener, the solids increase to 5%- 10% concentration. Poly-electrolytes are added in a mixing tank prior to the pressure belt filters solids. These increase the solids to 20%-25% in the de-watered sludge. The total amount of sludge generated at this stage is 2,000 tonnes per annum. A new sludge dryer has been installed which will reduce the total sludge to 500-600 tonnes per annum and 90% solids from the sludge dryer.The dry sludge is disposed of to land fill. All filtrate from the belt filters and dryer are returned to the equalization tanks. Problems with Hydrogen Sulphide in the primary stages are

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controlled by the addition of a product called Odourblock Fe which is Ferric Nitrate based. This works in two ways

- The Fe ion combines with the sulphide to form Iron Sulphide a water insoluble compound. This has the effect of eliminating the bad odour and also prevents essential trace metals from being precipated.
- The Nitrate ion preferentially operates as an oxygen donor and prevents further sulphate reduction and associated Hydrogen Sulphide production. This system worked well for the company and they were pleased with it, the dosing rates could be set up in automatic mode.They had an outside contractor who visited the plant every few weeks to monitor the dosing system and control stocks.

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## 2.7 Limerick County Council Treatment Plant.

### 2.7.1 Introduction

The city of Limerick has over 70,000 people living within a 3 mile radius of the city centre. There are 15.000 house holds within the city limits and a further 6,000 households in counties Clare and Limerick which use the city sewer system. Each household generates on average 150-250 gallons of waste water per day. Up to 2003 there was no waste water treatment facilities in the city until a new drainage scheme and water treatment plant was constructed. This new treatment will process 4 million gallons of waste water daily before discharging to the river Shannon. The EU Directive on Urban Waste Water requires that urban areas exceeding 15,000 population and located on estuaries be provided with a treatment plant to at least secondary treatment standard. It further requires a collection system designed to prevent untreated discharges into receiving waters and that the discharge of the treated effluent meets all relevant directives and national standards

(a).Preliminary Treatment

This involves the removal of debris, larger solids and grit by straight forward screen and settlement.

(b). Primary treatment

This again is a settlement process to separate solid material from the waste water. The remaining waste which now contains dissolved pollutants and non-settlement solid material is then transferred to the biological or secondary treatment phase.

### 2.7.2 Biological Treatment.

Large concentrations of micro-organisms are developed in tanks by mixing and continuously aerating to provide oxygen for the micro-organisms. These Aeration tanks reduce BOD and phosphorous levels and maintain an $O_2$ rich environment. There are six aeration tanks with a retention time is around ten hours. The next phase is the Secondary settlement tanks

### **2.7.3** Sludge Handling

The biomass is separated from the treated waste water which is suitable for discharging to the river Shannon. The solids concentration is increased by filter presses and thermal drying system The water content is reduced from 80-85% to 8% A useful by-product of the process is the bio-solids produced from the primary settlement and biological phases of the treatment process These solids have potentially very valuable properties containing nutrients such as nitrogen and phosphorous as well as trace elements essential for plant and animal growth. The bio-solids also have a significant calorific value which makes it the material potentially useful as a fuel for industry and power generation. In addition the pathogen free solids will be readily usable as farm fertilisers. They will be clean and safe to handle in a granular or pellet form which can be used in a conventional farmyard spreader. Besides the nutrient value it will improve the physical properties of the soil to which it is applied.

### **2.7.4** Waste Gases

The gases from the Sludge Tanks and the filter presses are routed to a Thermal Oxidiser This process consists of a regenerative thermal oxidation device with a high efficiency heat recovery system and a type of ceramic filling mass such to minimise the electric power consumption. The process is divided into phases during which each chamber becomes in succession inlet-chamber, purge-chamber and outlet chamber .

(a) The cold air to be cleaned in chamber 1 flows through the ceramic bed which has been heated up from the previous process interval, gives up its heat to the cold and polluted air and raises it to a temperature as close as possible to the reaction temperature which is about 800 $^0$c depending on the substances contained in the fluid to be treated. By continuously taking heat away from bed No1 the temperature falls in a significant way. The gaseous stream reaches the combustion chamber where the reaction temperature is achieved either by auto-ignition of the contaminates or by using additional fuel . The flue gas stays at the combustion temperature for one second. After leaving the combustion chamber the cleaned gas flows downwards in chamber No2. This way the gas at gives up its heat to bed No2.and is ready for following process sequence when flue gas to be cleaned flows into this chamber

(b) During this second phase chamber No.1 is cleaned. The polluted stream passes through No.2 in the same way and gives up its heat to chamber No.3; this sequence continues using the 3 chambers.

The advantages are:

- Flexibility both for waste air quantities and different solvent loads, the ceramic material due to its large volume can handle fluctuations in flows and concentrations
- Reduced generation of secondary contaminants NOx and $CO_2$ as the fuel consumption is low.
- Very low maintenance costs
- The use of ceramic materials reduces electric consumption.

The plant also has the facility to handle sludge from outside of the plant brought in by tanker. The tankers are connected to pipe work inside in a building which has an ionisation process. This method of ion generation involves the production of small ions both negative and positive which have excellent oxidation capacity. The small ions are generated artificially using a reactive plasma generator. The key component of the ion generator are the coronar discharge tubes which create an electronic field around the immediate area of the tubes when an electric current is passed through them. The input voltage can be varied by means of a step transformer with output of 2,900 Volts. The alternating current produces both negative and positive ions in a 5:4 ratio as found in the atmosphere. Fresh filtered air is passed over the tubes and the ionisation process converts the oxygen and hydrogen molecules to $O^-$, $O^+$, $H^-$, and $H^+$. The polarised air is then introduced to the foul air stream where organic chemical odours are oxidised to simpler forms. The oxidation will vary depending on:

- Molecular structure of odour compounds
- Concentration of the odour
- Contact time
- Ionisation level

The reaction with Hydrogen Sulphide will differ depending whether the reaction takes place over water. When Hydrogen sulphide comes into contact with O- the first oxidation reaction produces $SO_2$. If the reaction takes place over water the heavier than air $SO_2$ is rapidly absorbed back into the flow. If the reaction takes place without water the oxidation continues if sufficient contact time is given until the end product is sulphate and water. Ionisation as a rule will oxidise most organic compounds. This system can be used in sewers and will solve the problem of accelerated corrosion caused by humidity and Hydrogen Sulphide. The unit consists of a fan, filter, ionising unit and reaction chamber in an acoustic housing. It is effective on most sewage related odours such as mercaptans, amines, hydrogen sulphide, and ammonia.

### **2.7.5** Rising Mains

The Limerick Waste water Treatment plant, after start-up, had a problem with Hydrogen Sulphide odours in the mains which were solved in the early days of commissioning by adding liquid $O_2$ from a tanker. This was linked to pumping rates and they were adding 8kg of $O_2$ per hour. They now switch over mains every week and flush them with clean water which is working and enabled them to stop the oxygen addition.

Chemicals used in rising mains and sewage to prevent septicity and odours in sewers include oxidising agents for converting compounds to a more stable state thus reducing the odour nuisance and those which raise the oxidation potential land prevent reduction of sulphates, and bactericides which destroy or lower bacteriological activity. These chemicals include potassium permanganate, hydrogen peroxide, chlorine, ozone, oxygen.

Chemicals which raise the oxidation potential include oxygen, hydrogen peroxide and chlorine. The introduction of nitrate increases the redox potential and the mechanism of de-nitrification takes place with the release of nitrogen gas. Five electrons are required to go from the oxidised form of nitrogen (nitrate) through to nitrogen gas. These are provided by the carbon in the sewage.

## 2.8 Irish Sugar Company, Carlow

### 2.8.1 Introduction

Tour consisted of a visit to their main plant the water treatment system and the settling ponds. They have a total of eight ponds which they use for settling of solids and storage of effluent. They allow some ponds to dry out and then excavate out the solids which have come from the washings of the beet.

### 2.8.2 Irish Sugar Water Systems

Water is taken from the river Barrow, treated and used for their process requirements. They have a total of nine settling lagoons where cooling and solid settling is done prior to discharging back to the river. The following equipment is used in the effluent treatment process

- Intake screening and treatment
- Cooling Towers
- Cascade and Condenser systems
- Clarifier .
- Lamella Clarifier
- Anaerobic Digestor
- Hydrolysis Tank
- Heat Exchangers
- Gas return to Boilers
- Monashell Filter and Flare Stack

### **2.8.3** Anaerobic Digester Plant.

The primary source of effluent is the washing of the beet, the effluent load comes from the sugar which is leached from the beet and organic particles which also come from the beet and other vegetation. The water then is pumped to the clarifier where the mud is allowed settle and thicken while the supernatant overflows and is recycled back for beet washing.The thickened mud is pumped to lagoon No 1 where clay and mud settle. The overflow from No 1 passes to lagoon No 2 for more settling. The effluent from No 2 is controlled manually and pumped to No 3. The effluent from No 3 is pumped to the Anaerobic Digestor via a heat exchanger system and is heated to 37 $^{0}$C .This effluent is then fed to the Hydrolysis Tank where the pH drops to below 7.0 and acetogeneises takes place. The rate of feed is adjusted to give a very low food to mass ratio of 0.25 to 0.35 initially and gradually this is increased. The target is a figure of 1.0 .The F/M ratio is controlled by daily measurement of the volatile suspended solids {VSS} which when multiplied by the volume of the digester gives the mass[M} of sludge. The volume of influent multiplied by the COD concentration gives the food [F] fed into the system. The target at all times is to get the F/M ratio up to 1.0 while keeping the pH at 7.0.

The effluent then overflows from the hydrolysis to the digester where methanogenis takes place. Both the hydrolysis and digester tanks

- Are insulated
- Have central agitators
- Are piped to the common biogas system
- Operate on an overflow system.

The hydraulic capacity of the Digester is 6, 400m$^{3.}$ The overflow of the digester passes through a degasification vessel before entering the Lamella Separator where the sludge settles and is pumped back to the bottom of the digester. Excess sludge is pumped to lagoon No 1 where it settles with the clay.

The overflow from the Lamella separator cascades to a buffer tank from where the treated water is either returned to the transport water system at the clarifier or pumped to No 4 lagoon where it is stored with No 5,6,7,and 8 before being discharged to the river, The bio-gas can be returned to the boilers when the plant is on line or is passed through condensate traps and then flared to atmosphere.

The AD plant is designed to handle a hydraulic load of 3,800m$^3$/day and a biological load of 32t of COD /day The plant was seeded in 1999 with 500t of sludge from the municipal plant in Tullamore,

The plant is controlled on the following criterion;

| | |
|---|---|
| • Influent | temperature 37 $^{O}$C |
| • F/M ratio | 1.0 + or – 0.1 kg COD/kg VSS |
| • VSS | 5,000 mg/l |
| • Sludge volume SV 30 | 300 mg/l |
| • COD removal | 90% / 32t/day |
| • Bio gas –volume | 13,000m$^3$ /da |
| • Purity | 75% + |

The current biological loading is 60t/day in the effluent and the capacity of the AD plant is 32t/day which means processing 50% of the effluent in the campaign period . The remainder is stored in the lagoons and should be sufficiently broken down by the next season to be discharged to the river

### **2.8.4** The Monashell Process.

At the end of their process they have installed a bio filtration system supplied by Bord na Mona Environmental Ltd who offer a range of systems for the treatment of odour and VOC air borne emissions. The systems available from Bord na Mona include,

- **Monafil** ; This a peat based bio filtration system utilising media which offers a high removal efficiency for a wide range of odorous compounds.
- **Monashell** ; A biological system employing shell media which is suitable for the treatment of high and fluctuating levels of Hydrogen, mercaptans and alkyl sulphides.
- **Monashell Enhanced Bio-filtration [EBF]**
  A process which can treat high VOC levels from industrial processes
- **Monasorb;** Is a range of dry media systems delivering up to 99.9% Hydrogen Sulphide removal.

Irish Sugar Company are concerned about odour and complaints from the public and at times are dependent on wind direction to avoid complaints from Carlow residents. There were 13 complaints to the Environmental Protection Agency last year, even though the plant is shut down for eight months of the every year. In the past four years they have installed an anaerobic digester and Monashell Bio filtration system and are supplying gas from the system to fuel their boilers with approx savings of 20% in fuel The Hydrogen sulphide gas from the Lamella Separator and the buffer tank is drawn off and put through the Monashell Bio filter.

In all conventional bio- filters, the biological conversion of Hydrogen Sulphide results in the production of mild sulphuric acid which if allowed to build up will acidify the support media and result in low abatement performance .

Monashell is a biological system which utilises media with an ability to control variations in pH by neutralising acid by-products which form as a result of biological oxidation of Sulphur compounds. This allows for the treatment of high levels of Hydrogen Sulphide and reduced Sulphur compounds .The process is also assisted by optimum pH ranges on the surface of the packing which enhances capture and breakdown of low solubility reduced sulphur compounds such as alkyl sulphide and mercaptans.

### 2.8.4.1 Media

Monashell consists of shells coated with a blend of specifically selected micro-organisms selected for its ability to degrade high levels of Hydrogen Sulphide. The shells contain a high level of $CaCo_3$, which neutralises acid as it is produced as a result of bacterial oxidation of sulphides. The process is further enhanced by the physical structural and chemical properties of the media which allows for smaller filters with high efficiencies and improved elimination abilities. The process is also proving extremely effective for the treatment of VOC and nitrogen based compounds.

### 2.8.4.2 System Design.

Monashell is erected on a prepared concrete plinth. The housings are constructed from glass reinforced plastic [G.R.P.], bolted panels, and plenum floor, filter media, irrigation system, heavy duty cover, inlet and outlet connections and access ports. The heavy duty covers are removable for media changes and irrigation nozzles are accessible from the filter cover. All internal components are constructed from corrosion resistant materials

| **Compounds** | **Concentration Range** | **Removal Efficiency** |
|---|---|---|
| Odour | Up to $10^6$ ou/$m^3$ | 99% |
| VOC | 200 to 2000 mg/$m^3$ | 90% |
| Hydrogen sulphides | 5 to 2000mg/$m^3$ | 99% |
| ammonia | Up to 100 ppm | 98% |
| Organic sulphides | Up to 200mg/$m^3$ | 95% |

Table 2.2. Monashell Performance Criteria (soucre Bord na Mona, Clean air Solutions)

**Benefits**

- Ability to treat high levels of Hydrogen Sulphide and organic Sulphides.
- High efficiencies.
- Low running costs .
- Lower footprint than conventional bio- filters.
- Sustainable process utilising natural occurring media.
- Very high performance on broad range of compounds.
- Ability to treat high variable inlet concentrations.
- Offsite or on site modular construction for ease of installation. The Sugar Company have the Monshell in place for 4 years and have not had to change the media.

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## 2.9 Dundalk WWTP.

### 2.9.1. Introduction

The information on the Dundalk Waste water treatment plant was received from the commissioning engineer of the company who built the plant. The hydrogen sulphide odours have been a problem for over two years The odour problem in Dundalk comes from the rising mains which are over 3km long coming from the town. The summer months were the worst which required the installation of a dosing system. They dose Neutroix TM which is nitrate based. The dosing rate is linked to the pumping rates which can be as high as 5,000m$^3$/day.Usage has been 5 tonnes per month over the winter months at a cost of 50cent per litre. The flushing of the mains has not been successful as with the Limerick plant and the difference is thought to be due to the length of the mains.

### 2.9.2. Problems in other Sewage Systems

Anglian Water Services the largest Water Company in England and Wales have had odour problems in a number of plant including Woburn, Boston, Walton-on-Naze and Colchester. They have conducted trials on these plants using a number of chemicals to combat odour and septicity problems, these include: ferric salts, ferrous salts, chlorine gas, hydrogen peroxide, sodium hypochlorite, nitrate salts, bulk oxygen, potassium permanganate, bio-augmentation, ozone, and re-odorant spray. Their conclusions were as follows:

*"Although there are a wide range of chemicals and systems available for prevention of and the treatment of odour and septicity problems, the selection of chemicals is driven by preventive or curative measures and costs. A better understanding of nitrates has led to their greater use sometimes it is necessary to use a combination of treatment systems to eliminate odour nuisance*(Sercombe, *1995)"*

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# 3.0 Trial at the Aughinish Alumina Effluent plant

## 3.1 Introduction

A waste effluent treatment system was installed in order to dispose of excess water from the plant into the river Shannon in an environmentally acceptable manner. The existing consent limits for effluent discharged to the Shannon require a pH of 6.0-8.5, a suspended solids concentration less than 50 mg/l and a temperature less than 20 °C in the receiving waters. The effluent treatment comprises three unit operations, neutralisation, clarification and cooling. The latter is accomplished by natural cooling in the South Pond and in the Liquid Waste Pond (LWP), which is located outside Area 34, adjacent to the Storm Water Pond (SWP). This section of the plant comprises a sequence of ponds and tanks namely the South Pond, the Waste Effluent Disposal Tank (WEDT), the Buffer Tank, the Effluent Clarifier, the Spent Acid Tank and the Fresh Acid Tank.

**Plate 3.1 South Pond which provides storage capacity for clarifier feed water.**

**Plate 3.2** **Clarifier on the right and buffer tank on the left with associated piping.**

Excess water streams, such as water from the storm water pond (mud stack run-off), East and West Pond (plant rain water collection ponds), cooling tower bleed, excess condensate, and all waters from the plant are collected as effluent in the South Pond. The South Pond provides a storage facility for all plant process effluents converging with a flow averaging 400 $m^3/h$. The effluent is neutralised in two stages using dilute sulphuric acid. The first stage is carried out in the WEDT to a pH of about 9.0 with spent acid from heater cleaning or fresh acid, supplied from the fresh acid tank. The WEDT overflows by gravity to the Buffer Tank, where the effluent is trim-neutralised to pH 7.0-7.5 with fresh acid from the Fresh Acid Tank.

The neutralisation is accompanied by precipitation of fine (gelatinous) aluminium hydroxide particles. The particles are removed by flocculent aided sedimentation in a clarifier. The clarifier is gravity fed from the Buffer Tank and feeds the clarifier which in turn overflows via a pipeline to the Liquid Waste Pond. A sludge blanket level detector is installed on the clarifier to aid in the control of solids in the overflow to the LWP. The sludge is recycled on a continuous basis and excess underflow sludge from the clarifier, containing the settled solids, is pumped back into the process. The flow from the LWP in Area 54 is pumped directly to the Shannon.

## 3.2 The Problem

The neutralisation process generates significant quantities of sodium sulphate salts approximately 4.2 tonnes per day (dry solids). These sulphate salts are reduced by sulphate reducing bacteria (SRB) as the system has a low dissolved oxygen (< 0.5 mg/l $O_2$) resulting in sulphide production and associated odour and settlement problems. The generation of the sulphide releases sulphide gases in the form of microscopic bubbles which attach themselves to the solids generated in the process and result in significant carryover of solids. The carryover of solids settle in the LWP and thereby create the costly exercise of LWP cleanouts and odour problems associated with stagnant ponds.

## 3.3 Experimental Programme

The technologies available to Aughinish Alumina were investigated under the heading of:

- Cost (capital and operational)
- Proven track record
- Known technology details from suppliers

It was decided that the addition of bacteria to bio-augment odours created by hydrogen sulphide would be trialed. The product selected was '*BIO-TREAT OC*' this product is sait to inhibit the formation of malodours ($H_2S$) from waste and waste water. It does this by breaking down odour causing compounds through hydrolysis and bio-oxidation; in short the sulphide is concerted to sulphuric acid.

$$2S^{2-} + 30_2 \rightarrow 2S0_3\text{-}+ \quad 2H_20 \rightarrow 2H_2SO_4$$

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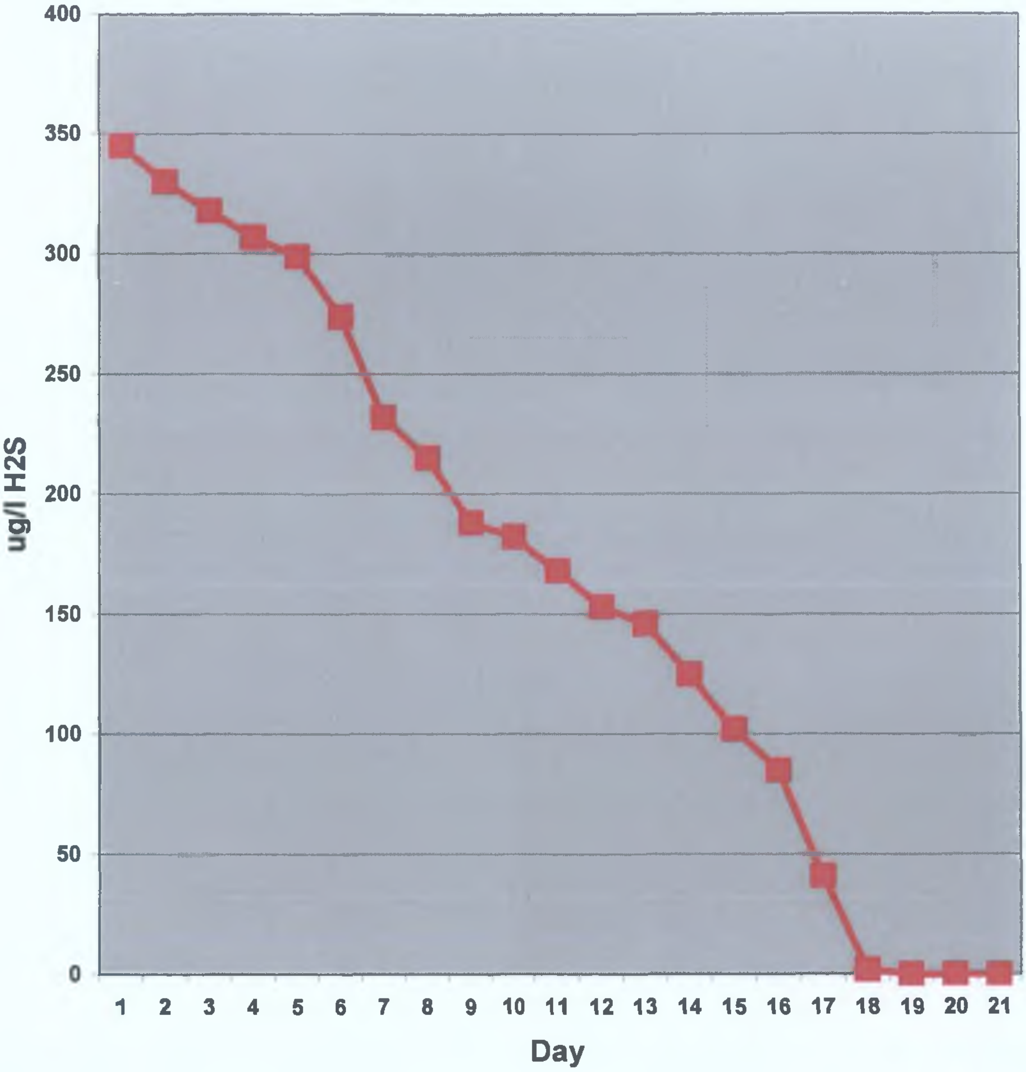
**Plate 3.3** **The Bio-reactor installed to determine effiectiveness of bacterial addition to remove hydrogen sulphide**

The bio-treat OC is principally used in environments that have low dissolved oxygen. 45 litres of clarifier underflow was dosed with Bio-Treat OC on day zero. The sample was then stored at temperatures of 17-19°C. The evolved Hydrogen Sulphide was displaced and trapped daily. The graph 7.1 below shows the level of Hydrogen Sulphide µg/l evolved over each 24 hour period of the 21 day survey.



**Graph 3.1: Hydrogen Sulpide Concentration in Clarifier underflow amended with Bio-Treat OC.**

## 3.4 Results

### 3.4.1 Background Hydrogen Sulphide

The background sulphide production was determined before commencement of bacterial bio-augmentation of sulphide. was a good relationship between solids content and sulphide concentration, therefore by maintaining a low solids in the clarifier underflow odours can be minimised. The analysis of hydrogen sulphide concentrations in the clarifier underflow was carried out for four weeks as shown in Table 3.1 below. This was part of the project to determine sulphide concentrations and thereby determine possible solution to the problem. The level of sulphide was dependent firstly on the solids content of the under solids. There was a good relationship between solids content and sulphide concentration,therefore by maintaining a low solids concentration in the clarifier underflow odours can be minimised.

| **Date** | **µg/l $H_2S$** | **% Solids** | **Bacterial Population /ml** |
|---|---|---|---|
| 12/01/ 04 | 453 | 3.2 | 1.00E+02 |
| 13/01/04 | 443 | 3.12 | 1.00E+02 |
| 14/01/04 | 440 | 3.18 | 1.00E+02 |
| 15/01/04 | 490 | 3.45 | 1.00E+02 |
| 16/01/04 | 487 | 3.42 | 1.00E+02 |
| 19/01/04 | 479 | 3.43 | 1.00E+02 |
| 20/01/04 | 458 | 3.49 | 1.00E+02 |
| 21/01/04 | 390 | 3.01 | 1.00E+02 |
| 22/01/04 | 438 | 3.43 | 1.00E+02 |
| 23/01/04 | 445 | 3.89 | 1.00E+02 |
| 26/01/04 | 367 | 3.21 | 1.00E+03 |
| 27/01/04 | 391 | 3.48 | 1.00E+02 |
| 28/01/04 | 404 | 3.54 | 1.00E+02 |
| 29/0104 | 423 | 3.68 | 1.00E+02 |
| 31/01/04 | 349 | 3.36 | 1.00E+02 |
| 2/02/04 | 335 | 3.55 | 1.00E+03 |
| 3/02/04 | 350 | 3.01 | 1.00E+03 |
| 4/02/04 | 254 | 3.52 | 1.00E+04 |
| 5/02/04 | 302 | 3.38 | 1.00E+04 |
| 6/02/04 | 342 | 3.3 | 1.00E+04 |

**Table 3.1** Hydrogen sulphide concentrations and solids content in clarifier underflow over a four week period.

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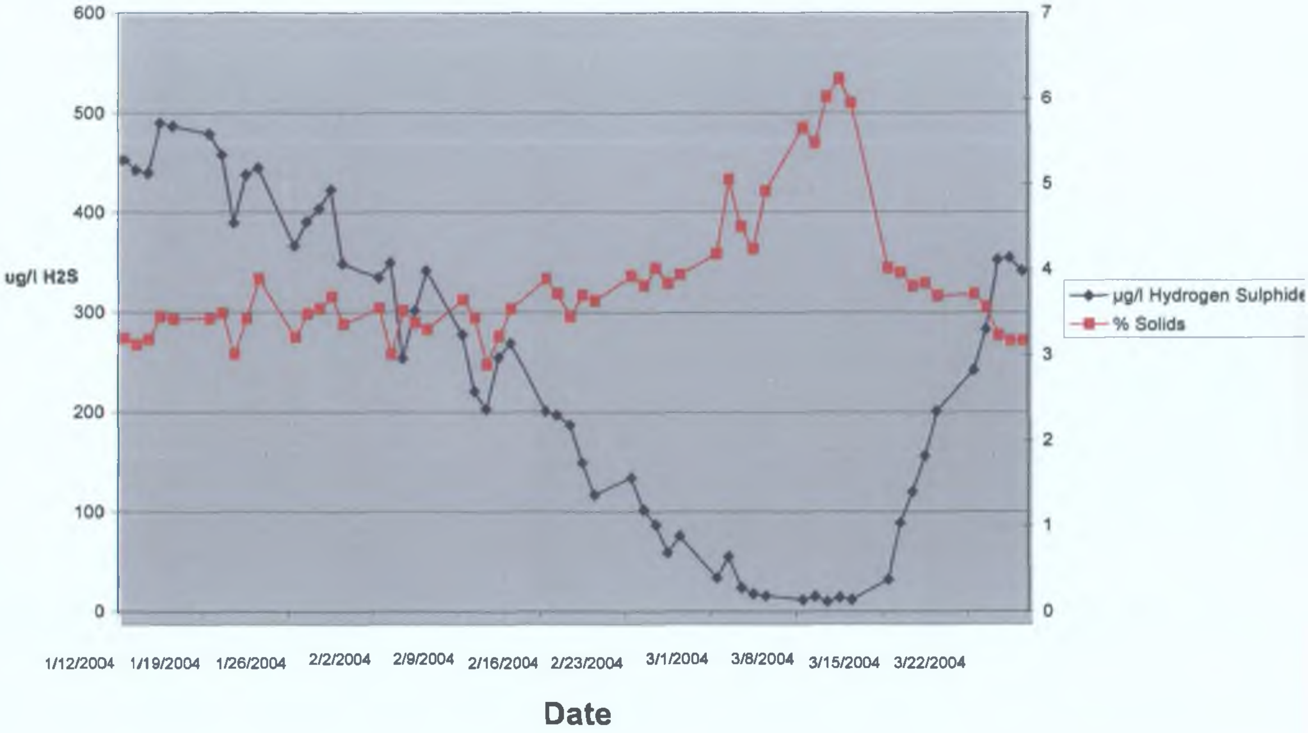
### 3.4.2. The effect of bacterial addition.

By installing a Bio-Treat Unit at the Plant, a large volume of concentrated bacteria was cultured. At the start of each 24-hour growth cycle 100 millilitres inoculums and 1 litre of nutrient (food source) was added to 200 litres of clean freshwater. After 24 hours in a temperature-controlled environment and with continuous aeration, the bacterial population grew up to a concentration of bacteria of $10^{12}$.This was continued for 8 weeks.

| Date | µg/l $H_2S$ | % Solids | Bacterial Population /ml |
|---|---|---|---|
| 9/02/04 | 278 | 3.65 | 1.00E+04 |
| 10/02/04 | 221 | 3.44 | 1.00E+04 |
| 11/02/04 | 203 | 2.89 | 1.00E+04 |
| 12/02/04 | 255 | 3.22 | 1.00E+04 |
| 13/02/04 | 269 | 3.54 | 1.00E+04 |
| 16/02/04 | 201 | 3.89 | 1.00E+05 |
| 17/02/04 | 197 | 3.72 | 1.00E+05 |
| 18/02/04 | 187 | 3.45 | 1.00E+05 |
| 19/02/04 | 149 | 3.7 | 1.00E+06 |
| 20/02/04 | 117 | 3.63 | 1.00E+06 |
| 23/02/04 | 134 | 3.92 | 1.00E+06 |
| 24/02/04 | 102 | 3.81 | 1.00E+06 |
| 25/02/04 | 87 | 4.01 | 1.00E+06 |
| 26/02/04 | 59 | 3.83 | 1.00E+06 |
| 27/0204 | 76 | 3.94 | 1.00E+06 |
| 1/03/04 | 34 | 4.18 | 1.00E+07 |
| 2/03/04 | 55 | 5.05 | 1.00E+07 |
| 3/03/04 | 24 | 4.5 | 1.00E+07 |
| 4/03/04 | 18 | 4.24 | 1.00E+07 |
| 5/03/04 | 16 | 4.92 | 1.00E+07 |
| 8/03/04 | 12 | 5.66 | 1.00E+07 |
| 9/03/04 | 15 | 5.48 | 1.00E+07 |
| 10/03/04 | 10 | 6.02 | 1.00E+07 |
| 11/03/04 | 14 | 6.23 | 1.00E+07 |
| 12/03/04 | 12 | 5.95 | 1.00E+07 |

**Table 3.2** Solids loading in the clarifier versus Hydrogen sulphide and bacterial populations over the trial period.

The solids level ranges from 2 to 9% but the design specification of the clarifier is 20% solids Large quantities of Hydrogen Sulphide are produced when the solids are at 7%. The addition of the bacteria did reduce the production of Hydrogen Sulphide and this in turn led to an improvement in the solids retention by the clarifier and reduded the solids in the overflow. This is demonstrated in the graph below (Graph 3.1), when solids concentration rises the sulphide concentration follows and vice versa.

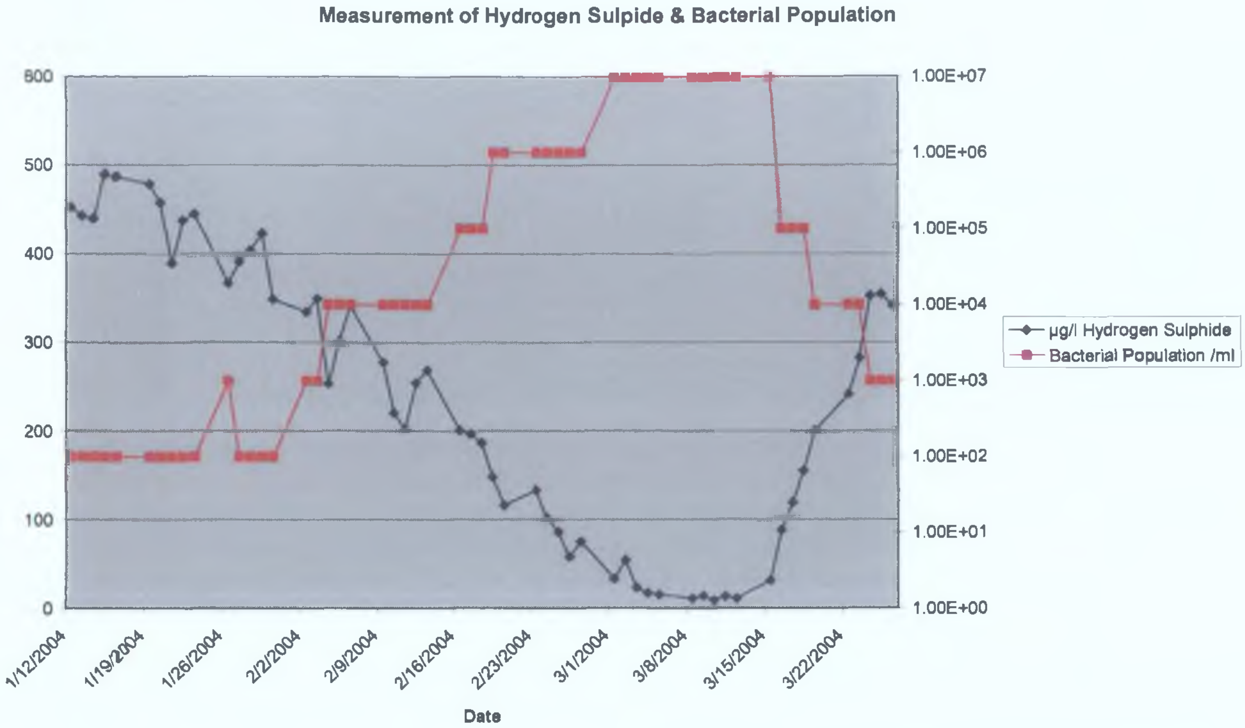


**Graph 3.2** - Measurement of Hydrogen Sulphide & Percentage Solids in Clarifier underflow

The bacterial addition was stopped for 2 to 3 weeks to determine the effect of removing Sulphide measurement was contiued for 2 weeks after cessation of bacterial addition.

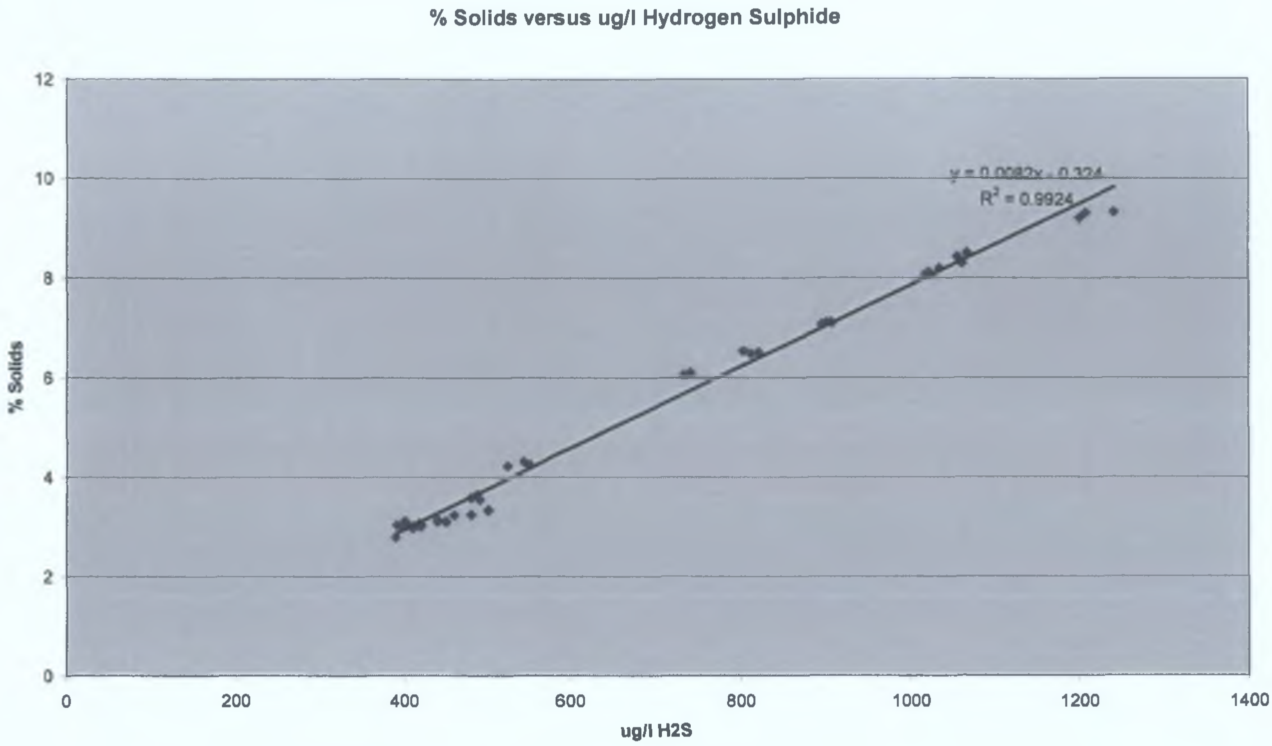
| **Date** | **µg/l $H_2S$** | **% Solids** | **Bacterial Population /ml** |
|---|---|---|---|
| 15 March 2004 | 32 | 4.01 | 1.00E+07 |
| 16 March 2004 | 89 | 3.96 | 1.00E+05 |
| 17 March 2004 | 120 | 3.8 | 1.00E+05 |
| 18 March 2004 | 156 | 3.84 | 1.00E+05 |
| 19 March 2004 | 201 | 3.69 | 1.00E+04 |
| 22 March 2004 | 242 | 3.71 | 1.00E+04 |
| 23 March 2004 | 283 | 3.56 | 1.00E+04 |
| 24 March 2004 | 353 | 3.23 | 1.00E+03 |
| 25 March 2004 | 355 | 3.17 | 1.00E+03 |
| 26 March 2004 | 342 | 3.17 | 1.00E+03 |

Table 3.3 Showing the hydrogen sulphide, bacterial population and solids concentrations after the addition of Bio-treat OC ceased.



Graph 3.3 Concentration of hydrogen sulphide and bacterial populations as population of bacteria increases the concentration the sulphide decreases and vice versa.

The percentage solids in the clarifier underflow have a direct relationship with the hydrogen sulphide concentration. The regression line (an R value of 0.992) shown in the graph below (Graph 3.3) show there is a excellent relation between the two.



**Graph 3.4 Comparison of hydrogen sulphide and solids concentration without bacterial addition**

The installation of the Bio-Treat system has achieved a definite improvement in the operational efficiencies of the 35 metre clarifier. The solids recycle is needed for operational control but odour problems meant that the operational efficiencies desired were not achieved. This was particularly evident when the solids recycle increased above 5%.

With the installation of a permanent Bio-Treat OC addition system clarifier under flow solids of 15% are achievable and in turn considerable improvement in the solids level in the clarifier overflow will be recorded.

The microbial additions program reduced the production of odours, improved the management characteristics of the sludge recycle and reduced the amount of odours produced.

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## 4.0 Discussion

Hydrogen sulphide ($H_2S$) is a dissolved gas that gives water a characteristic "rotten egg" taste and odour. It corrodes piping creates odour and turns water black. Hydrogen Sulphide can cause odour problems at a concentration level as low as 0.05 mg/l.

The incidence of odour nuisance complaints is on the increase. This is due in part to increased public sensitivity to odours as well as the need to build ever closer to the sources of odour. What were once sewage works and industrial facilities several miles from the outskirts of towns are now surrounded by suburbia industrial parks, superstores and residential areas. This has increased the likelihood of complaints since the enactment of the Environmental Protection Agency Act, 1992, which includes odour as a statutory nuisance. It means that the inclusion of odour control measures in both the design and retrofitting of existing plant is vital.

Odours can not be completely removed. In fact it is not necessary to do so. What is required is to reduce the impact of the odour to a level where it does not cause a problem. This can be done by reducing the volume of air emitted or reducing the odour of the air released.

A reduction in the volume of air can, in its simplest form, be achieved by covering the air source and extracting the air from that area alone. Another approach is the serial use of air by taking the air from less odorous areas and using this to sweep odours from the most odorous areas. The strength of the odour can be reduced by treating the air stream. A wide range of systems are available and are discussed in the next section. Often a combination of these two approaches is used. Covering to reduce the air volume needing treatment (not necessarily the overall 'odour load') and treatment to reduce the odour concentration.

There are a four basic approaches to odour control currently used, these are physical, chemical, biological, and thermal. Containment is one method and can include the

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following: installation of covers, collection hoods and air handling equipment for containing and directing odorous gases to disposal or treatment systems The pollutant concentration must not exceed 10% of the LEL inside the enclosure E.P.A.(2002). Gases can be mixed with fresh air sources to reduce the odour unit values. Alternatively gases can be discharged through tall stack to achieve atmospheric dilution and disperion. Gaseous odours can eliminate by combustion at temperatures varying from 650 – 815 °C. gases can be combusted in conjunction with treatment plant solids or separately in a fume incinerator. It has the advantage of being almost universally applicable as a method of odour control because all organic odours can be oxidised if the temperature is raised high enough E.P.A.(1995). Temperatures can be brought to $1000^{0}$ C if necessary Gay (1997),however high capital and operating costs migitage against this system compared to other abatement systems. Odorous gases can be passed through bed of activated carbon to remove odours.

Carbon regeneration can be used to reduce costs.Activated carbon treats odours and adsorbs molecules into its porous surface. The size of the molecules adsorbed relates to the size of the pores available. Since most of the odours created at wastewater treatment plant are small molecules, this necessities an activated carbon with a large number of small pores. This is difficult to obtain. Some manufacturers have impregnated the carbon with chemicals such as iodine to partially oxidise so components to species that are more readily adsorbed and hence over come the problem. Carbon has only a finite number of pores of the correct size for the odour molecules and therefore the media requires replacement at regular intervals. Activated carbon is commonly fitted in a wide range of environments either as a passive vent filter or an activated filter. Humidity is an important factor. If it exceeds 85%, the carbon performance can be reduced and increase running costs Cha, (1999). Above these levels a liquid film forms over the surface of the carbon reducing the adsorption rate which in turn leads to the need for a higher retention times than that required at lower humidities.

Carbon systems have high removal efficiencies when designed properly and enjoy a large market share. Odorous gases can be passed through sand, soil, or compost beds. Odorous gases from pumping stations maybe vented to the surrounding solids or to specially designed beds containing sand or soil. Odorous gases collection from treatment units maybe passed through compost beds. The important parameters are even distribution over the bed, keeping the filter media moist at all times (Van Langenhove, 1996) and maintaining pH above 3 in order not to decrease the biodegration of the Hydrogen Sulphide (Yang and Allen ,1994).The injection of air or pure oxygen or Ozone into the wastewater to control the development of anaerobic has proven to be effective. Oxygen addition will prevent septicity, oxidise sulphide and promote bio-oxidation of sulphide. Ozone treatment involves the use of Ozone ($O_3$) a reactive gas and powerful oxidising agent. It can kill odour causing bacteria and can react with Hydrogen Sulphide like other oxidisers such $H_2O_2$. Substantial energy is required to produce Ozone. An Ozone generator is usually set-up on site that consists of three sub-systems, feed gas preparation, Ozone generation and Ozone water contacting. These are only effective in a narrow spectrum of odour control, however, as the gas requires major installation this type of system is prohibitive. There can be some advantages due to some improvements in colour ,and turbidity when used in tertiary treatment plants (Balakrishnan, 2002)

Masking agent can be used for malodours. Usually masking agents are a short term control only. They are used to over power or mask objectionable odours. In some cases the odour of the masking agent is more offensive than the original odour. Effectiveness of masking agents is limited. The application of masking agents can become dangerous if they mask the odour of high and toxic concentrations of gases. Also when dilution of the masking agent to below its threshold value occurs before the the malodorous compounds have reached their odour thresholdvalue problems can arise at a certain distance from the source (Anderson, 1998). Complaints can arise if residents of an area notice a different odour even though the new odour is not offensive..

Odorous gases can be passed through specially design scrubbing towers to remove odours. If the level of carbon dioxide is high the cost can be prohibitive.
The effectiveness of chemical scrubbing is directly proportional to the extent to which the odorous species can be both identified and quantified carefully balancing of the reagent to the odorous species is essential. In most cases it is essential to use a two stage unit, where an alkaline stage is used to remove Hydrogen Sulphide and organic acids. For the

treatment of Hydrogen Sulphide alkaline is considered the most efficient type scrubbing (Weast ,1976). An acid stage is used to remove components such as amines and mercaptans. Some systems used catalysts to reduce the size of the system and the chemical demand. Highly basic and acid residues are generated and these require treatment before disposal which will add significantly to the operating costs.

The process has been used to de-odorise air in a very wide range of industries and is the most common system for treating large volumes of air. Some wet chemical scrubbing systems have been installed at wastewater treatment plants especially where steady and high levels of hydrogen sulphide have been generated.

The two most commonly used alkalis (magnesium hydroxide - $Mg(OH)_2$ and sodium hydroxide - NaOH) are supplied as a slurry and solution, respectively, the former in bulk truckloads and the latter in a range of container sizes as well as bulk truckloads. Oxidising the odour compound in wastewater is one of the most common methods used to achieve odour control. Chlorine, Ozone, Hydrogen peroxide, Potassium Permanagate are among the oxidants that are used. Chlorine also limits the development of a slime layer. Hydrogen peroxide scrubbing is being used more in recent times in preference to the more commonly used sodium hypochlorite becauseit is more cost effective due to storage and transport costs. It is also considered to be more suited to warmer climates (Tomar,1994)

All oxidizing agents require filtration after use and will increase costs. The commonly used oxidizing scrubbing liquids include chlorine, sodium hypochlorite, sodium hydroxide, potassium permanganate, nitrites, metallic salts, iron salts, ozone, chelated iron, and scrubbing with alkalis. Other agents include magnesium hydroxide, magnesium oxide, ferric sulphate, ferric chloride, ferric iron. Nitrates such as sodium or calcium nitrate have long been used as inhibitors to control odours. One advantage of nitrate inhibitors is that they prevent the formation of undesirable by-products such as Hydrogen Sulphide from biological metabolism. Another is that odour may be prevented at relative low product dosage rates. Facultative and obligate anaerobic bacteria, which are responsible for sulphide and odour production prefer nitrate to sulphate as electron acceptors during cell metabolism.

The process registered as the “Nutrior $^{TM}$ Process” and during a trial at a Norsk Hydro plant in Norway resulted in reduction from 4.2 mg/l to 0.24 mg/l sulphide after dosing. With a break through of nitrate to the treatment plant, BOD removal was also increased across the rising main. Hydrogen sulphide is removed from condensate in wastewater plants by adding chelate or liqand (L) usually EDTA which increases the solubility of iron in the water which in turn reacts with the dissolved Hydrogen Sulphide (Nagl, 2002) This process involved the adding of EDTA and Iron (Ferric Fe+3) the iron oxidises the Hydrogen sulphide to sulphur.

- $2\ Fe^{+3} \quad + \quad H2S \quad \rightarrow \quad 2Fe^{+2} \quad + \quad S^0 \quad 2H^-$

The ferrous Iron needs to be reused in order to reduce operating cost is re-oxidised.

- $2\ Fe^{+2} \quad + \quad \frac{1}{2} O_2 + \quad 2H^- \quad \rightarrow \quad 2Fe^{+3} \quad + \quad H_20$

The element sulphur produced in the above reaction must be removed in order to prevent the system blocking up. This to done by adding sodium sulphite thereby producing sodium thiosulphate

$$S^0 \quad + \quad Na_2SO_3 \quad \rightarrow \quad Na_2SO_4$$

Biological conversion involves the used of naturally occurring microbes to oxidise odorous compounds in the air stream. In practice this involves sulphur oxidising bacteria for the removal of Hydrogen Sulphide and other species for the removal of organic odour components. Two approaches are mainly used bio-filters and bio-scrubbers. Bio-scrubbers are the biological analogue of counter current gas scrubbers. Here a micro-biological film is immobilised on the gas/liquid transfer media.
A bio-filter is the gas treatment equivalent of a percolating filter. In this system

- the media has the combination of a very high surface area to support the microbes
- a low pressure loss to reduce air movement costs.

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The choice of systems depends on both the composition and strength of the odour. High Hydrogen Sulphides loading are best treated using a bio-scrubber where the microbes can be carefully selected to include a high proportion of bacteria that utilise hydrogen sulphide as there energy source. Combinations of high organic content coupled with relatively low hydrogen sulphide loading are treated with a bio-filter. However bio-filters occupy significantly more land area for the same duty for the equivalent bio-scrubber.

Biological system posses advantages over other systems in that the activate ingredients are both replicating and self regulating. The bio-filters system will adapt to changing odour composition by changing both the number and type of microbes present. The same approach enables the bio-filter to be used on a wide range of odours often without detailed knowledge of the odour components. However all bio-reactor systems are sensitive to changes in temperature and humidity (Sergeleldin, 2001). Biological plant has been used for the treatment of malodorous air from sewage treatment works and their sludge handling systems as well as a wide range of effluent treatment plants. It has also been installed in a wide range of air steam as diverse as chicken processing through to pharmaceutical plant to fine chemical manufacturing to food processing.

Specially designed towers can be used to remove odorous compounds. Typically the towers are packed with plastic media of various types on which biological growth can be maintained. These towers can be selected to contain a high proportion of bacteria that utilises Hydrogen Sulphide as their energy source. Some claim up to 99% efficient but according to (Burgess *et al.* 2001) who did a review of sludge in bio-scubbers it maybe too early to come to this conclusion due to insuffient data. There is no doubt that bio-systems can oxidise single pollutants or mixtures of pollutants in an air stream but the technology needs more development.

The clarifier was installed in 1993 and had been a significant source of odour, the implementation of the trial has reduced the number of complaints by operators working at the clarifier. The results demonstrate that the addition of the Bio-Treat OC had successfully reduced the concentration of hydrogen sulphide in the clarifier under flow solids from a highly odorous and black solids to a non-odorous and white to pink solids. When the bacteria addition was terminated on the 12/03/2003 the bacterial population started to decline and the hydrogen sulphide concentration began to increase. Within a two week period the sulphide concentrations had returned to pre-trial levels.

Incineration, like carbon adsorption, is one of the best known methods of industrial gas waste disposal. Incineration is an ultimate disposal method in that the objectionable combustible compounds in the waste gas are converted rather than collected. A major advantage of incineration is that virtually any gaseous organic stream can be incinerated safely and cleanly, provided proper engineering design is used. The heart of an incinerator system is a combustion chamber in which the VOC-containing waste stream is burned. Since the inlet waste gas stream temperature is generally much lower than that required for combustion, energy must be supplied to the incinerator to raise the waste gas temperature. The energy released by the combustion of the odorous compounds in the waste gas stream is not sufficient to raise its own temperature to the desired levels, so that auxiliary fuel (e.g., natural gas) must be added.

The combustion of the waste gases may be accomplished in a thermal incinerator or in a catalytic incinerator. In the catalytic incinerator a catalyst is used to increase the rate of the combustion reaction, allowing the combustion to occur at lower temperatures. Because the catalytic process operates at a lower temperature than the thermal process, less auxiliary fuel may be required in the catalytic process to preheat the waste gas.

There are a number of different incinerator designs. These designs can be broadly classified as thermal systems and catalytic systems. Thermal systems may be direct flame incinerators with no energy recovery, flame incinerators with a recuperative heat exchanger, or regenerative systems which operate in a cyclic mode to achieve high energy recovery. Catalytic systems include fixed-bed (packed-bed or monolith) systems and fluid-bed systems, both of which provide for energy recovery. Both the thermal and catalytic incineration systems are designed to provide odour control through combustion at a level in compliance with applicable Irish and EU requirements.

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Given the wide range of options available, however, it is obvious that not every incinerator will fulfill these requirements at the same cost. This presents a first step toward deciding how best to deal with odour emission abatement using incinerators considering some qualitative factors pertinent to the types of incinerators described in this thesis. The following factors relating to the presence of contaminants should be considered by potential users (Grelecki, 1976).

The fouling of the catalyst in a catalytic system is a possibility. Poisons to the system include heavy metals, phosphorous, sulphur and most halogens, although catalysts have been developed that are chlorine resistant. The possibility of process upsets that could release any of the above poisons or cause fluctuations in the heating value to the incinerator would favour a thermal system. Except for the No.2 grade, fuel oil should not be considered as auxiliary fuel to a catalytic system due to the sulphur and vanadium it may contain (Sheffer, 1988).All of the above factors would serve to increase the operating expense of a catalytic unit through replacement costs of the catalyst. An additional factor relates to relative energy efficiency of the various types of incinerators:

Thermal units generally require more auxiliary fuel than catalytic units and operate at temperatures that are roughly 400°C higher. This difference in fuel requirement increases as the heating value of the waste stream decreases. In general, a trade-off exists between the higher capital costs of catalytic incinerators and the higher operating costs of thermal incinerators. Contaminant destruction efficiences of thermal incinerators typically range from 95%to 99% while catalytic units range from 90% to 99% .Catalytic units also can remove carbon monoxide from odour laiden air. E.P.A.(1995) Catalytic units operate at lower temperatures and hence lower fuel consumption (Paillard and Blondeau 1998). They also require smaller footprint.

## 5.0 Conclusion

In addition to Hydrogen Sulphide, volatile organic sulphur compounds which include Methylated sulphides (MeSH, $Me_2S$, $Me_2S_2$) and Carbon disulphide ($CS_2$) play an important role in the bio-geochemical sulphur cycle. Due to their very low odour threshold valve (ppbv range), high toxicity (TEL $< 20$ ppmv) and potential corrosive effect, the presence of these sulphur compounds in anthropogenic emissions source such as, composting, rendering and wastewater treatment plants should be kept to a minimum, or efficient abatement technologies are required to be installed.

In general, very high Hydrogen Sulphide elimination efficiencies can be obtained using both physicochemical (alkaline, Oxidative, catalytic scrubbing, AC adsorption), biochemical (Bio-filtration, bio-tricking filtration) and thermal (Catalytic, Regenerative, Recuperative, Direct flame incineration) methods. Special attention must be paid to the design of treatment systems with the intention of reducing obnoxious smells and designers must implement solutions to remove these sources. Moreover pilot plant experiments should be performed to select for each specific problem the optimal (combination of) abatement technology for optimal reaction conditions, which can, in combination with a through prevention strategy, control environmental problems caused by odorous compounds. Odour problems are likely to increase over the next ten years driven by greater public awareness and legislative pressure from national and EU fronts. A wide range of treatment method are available ranging from adsorption techniques with low capital and high running costs, through to biological systems with higher capital cost but low running costs. The choice of technique clearly depends on the application. However in many cases within wastewater treatment where high humidity and high organic loads are typical biological base treatment systems would appear to be the best choice.

The trial in Aughinish Alumina has been a success and has improved the operation of the clarifier and has also improved the working conditions for people on the plant.

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