

Land Contamination:
Technical Guidance on Special Sites:
Acid Tar Lagoons

R&D Technical Report P5-042/TR/04

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This report (P5-042/TR/04) is one of a series providing technical guidance on the complexities and characteristics of Special Sites as defined under the Contaminated Land (England) Regulations 2000 for Part IIA of the Environmental Protection Act 1990. Principally this document is for use by Agency staff carrying out regulatory duties under Part IIA, however this technical guidance contains information that may be of value to other regulators and practitioners dealing with Special Sites.

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FOREWORD

Part IIA of the Environmental Protection Act 1990 sets out a regulatory regime for the identification and remediation of land where contamination is causing unacceptable risks to defined receptors. The Environment Agency has a number of regulatory roles under this regime. Where land is designated as a Special Site, as defined in the Contaminated Land (England) Regulations 2000, the Agency will act as the enforcing authority. It is expected that a similar regime will be introduced in Wales during 2001, but the reader should check whether definitions of Special Sites in the Welsh regulations are the same as in the English ones.

The Environment Agency's approach to carrying out its regulatory responsibilities is set out in its Part IIA Process Documentation, available on the Agency website (www.environment-agency.gov.uk). This documentation sets out how the Agency intends to carry out its responsibilities under Part IIA of the Environmental Protection Act 1990, which came into force in England on 1 April 2000.

Users of the Part IIA process documentation should first refer to the Part IIA Process Handbook to obtain a clear understanding of the activities involved in the Part IIA regime, and with which Agency officer responsibility for particular tasks lies. The Procedures support the individual activities, and provide detailed step by step guidance on the necessary tasks. The Procedures are supported by Internal Standards which focus on the technical and legal aspects of the Part IIA regime. Other relevant advice is provided in Agency R&D documents and technical publications and in authoritative technical materials published by others including the Department of the Environment, Transport and the Regions.

This document is one of seven technical reports that provide background information about the categories of land designated as Special Sites identified in Regulation 2 of the Contaminated Land (England) Regulations 2000. The reports focus on the complexities and characteristics of the Special Site categories, and in particular, contamination types found specifically on these sites. The reports are not intended to provide regulatory or procedural guidance, but they aim to provide technical information to assist both Agency staff and others dealing with Special Sites in carrying out their work.

In the interests of transparency and openness, Part IIA process documentation, including this series of technical reports are made available to persons outside the Agency. They have particular relevance to local authorities, SEPA, DoE NI and to those affected by regulation under Part IIA.

GLOSSARY

Specific Technical Terms

Acid	A compound containing hydrogen (H), which on solution in water, produces an excess of hydrogen ions.
Acid Tar	Waste material produced as a by-product of certain petroleum refining processes, characterised by high molecular weight hydrocarbons and high acidic content.
Aliphatic	Pertaining to a straight carbon chain hydrocarbon.
Alkali	A compound, usually a soluble hydroxide of a metal, such as sodium hydroxide (NaOH), which on solution with water produces an excess of hydroxyl ions (OH ⁻).
Aromatic compounds	A type of hydrocarbon, such as benzene or toluene, with a specific type of ring structure.
Asphaltenes	High molecular weight tarry substances.
Auger	A tool resembling a large corkscrew used for boring holes.
Benzole	Unrefined compound used as fuel.
Bioavailability	The degree to which chemicals present in the soil matrix may be absorbed or metabolised by a human or ecological receptor.
Bioventing	Remediation technique which combines the processes of soil venting and <i>in situ</i> bioremediation.
Biodegradation	The breakdown of a substance or chemical by living organisms, usually bacteria.
Bioremediation	The use of biological methods to restore contaminated land.
BTEX	Benzene, toluene, ethylbenzene, xylenes.
BTX	Benzene, toluene and xylenes.
Carbonisation	Reduce to charcoal or coke.
Chemfix	A technique by which contaminants may be encapsulated in the soil using chemical solidification methods.
Corrosive	A chemical agent that reacts with the surface of material causing it to deteriorate or wear out.

Cresols	Colourless liquids or crystalline solids that occur in coal tar and cracked naphtha. They are volatile in steam and are reduced to toluene by Zinc dust.
Creosote	A dark brown oil distilled from coal tar, used as a wood preservative.
DCR	Dispersing by Chemical Reaction.
Desorption	Chemical dissociation from the surface of a solid or liquid.
Desulphurisation	Removal of sulphur.
Distillation	The act of purifying liquids through boiling, so that the steam or gaseous vapours condense to a pure liquid.
Direct Contact	Exposure to contaminants by touching with exposed skin.
Emulsion	A fine dispersion of one liquid in another.
Exothermic	Occurring or formed with the evolution of heat.
Extraction pit	An area used for the extraction of natural materials such as gravels or sands.
Fluidised bed Incinerator	An incinerator that uses a bed of hot sand or other granular material to transfer heat directly to waste.
Fuller's Earth	A clay consisting mainly of expanding smectites such as montmorillonite used industrially for its absorptive properties.
Hydrocarbon	Chemical compounds that consist entirely of carbon and hydrogen.
Hydrogen sulphide	Gas emitted during organic decomposition. Also a by-product of oil refining and burning. The gas smells of rotten eggs and in high concentrations can kill or cause illness.
Hydrophobic	Having a strong aversion to water.
Incineration	A treatment technology involving destruction of waste by controlled burning at high temperatures.
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention Control
Lagoon	Excavated or natural depression in the ground surface, forming an impoundment into which liquid material is placed.

Leaching	Dissolution of chemicals from waste materials into a liquid (typically water) and their subsequent removal away from the contaminated zone (e.g. towards groundwater).
Lime	Compounds mostly of calcium carbonates but also other basic (alkaline) substances.
Methane	A colourless non-poisonous, flammable gas creating by anaerobic decomposition of organic compounds.
Mercaptans	A group of organic compounds that contain sulphur (S) and are characterised by an offensive odours, sometimes likened to rotting cabbage.
Neoprene	A synthetic rubber-like polymer.
Neutralisation	Decreasing the acidity or alkalinity of a substance by adding alkaline or acidic materials, respectively.
Noxious	Harmful, unwholesome.
Oleum	Concentrated sulphuric acid containing excess sulphur trioxide in solution forming a dense corrosive liquid.
Organic acids	Acids compose of carbon (C) and (H) atoms.
Paraffins	Saturated aliphatic hydrocarbons with molecular formula C_nH_{2n-2}
PAHs	Polycyclic aromatic hydrocarbons. Complex, multi-ringed hydrocarbons of moderate to high molecular weight, moderate to low mobility in the environment and moderate to high toxicity.
Petroleum fractions	A fraction of crude oil products removed from the rest of the crude oil through distillation.
pH	The representation of the acidity or alkalinity of a substance on a logarithmic scale of 0 to 14 based on hydrogen ion concentration.
Phenols	Organic compounds that are by products of petroleum refining, tanning and textiles, dye and resin manufacturing.
Pneumatic	Containing or operated by compressed air.
Polymers	A natural or synthetic chemical structure where two or more like molecules are joined to form a more complex molecular structure.
PPE	Personal Protective Equipment
PTFE	Polytetrafluoroethene.

PVC	Polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
Selosafe	A remedial technique which concretes contaminants in place and prevents them from leaching.
Sodium salts	Salts containing the Sodium (Na) atom.
Sodium hydroxide	A compound which is strongly alkaline with chemical formula NaOH.
Solidified	To make or become solid.
Substrate	The surface or material on which any particular organism grows.
Sulphonate	A salt or ester of sulphonic acid; to convert into a sulphonate by reaction with sulphuric acid.
Sulphur dioxide	An acid gas in which each molecule contains one atom of sulphur (S) and two of oxygen (O). It is a product of the combustion of the materials containing sulphur.
Sulphuric acid	A dense oily colourless highly acid and corrosive liquid with a chemical formula of H ₂ SO ₄ .
Tar acids	Acidic compounds within tars.
Thermal	Systems that use elevated temperatures to induce physical and chemical processes such as volatilisation and combustion for eliminating toxic substances from the polluted soil.
Thermogravimetric	Type of analysis during which the percent weight loss is measured as a function of temperature.
Thiophenes	Sulphur-containing complex hydrocarbons, typically having low odour thresholds.
Thixotropic	Capable of changing from solid to liquid when agitated.
TPH	Total petroleum hydrocarbons. The mass of hydrocarbon present in a sample according to a specific analytical method (different methods give different results).
Viscosity	Physical characteristic of a substance which indicates how easily it flows and allows material to move through it.
VOCs	Volatile organic compounds.

Vitrification	Is related to solidification in that high temperatures are used to fuse contaminated materials into a glass or clinker material.
Volatilisation	The process through which compounds become volatile or vapours.
White oil	A liquid paraffin frequently used in medicinal preparations.
Xylenols	Hydroxydimethylbenzenes of which six isomers are possible. The pure substances are low-melting solids having the general properties of phenols. Xylenol is the name given to a mixture of the isomers separated from the phenolic fraction of coal tar.

1. INTRODUCTION

1.1 Background

This report is one of a series of technical guidance documents relating to Special Sites that are part of the statutory regime for contaminated land introduced by the implementation of s.57 of the Environment Act 1995 that added Part IIA into the 1990 Environmental Protection Act (EPA 1990). The application of this primary legislation is via the Contaminated Land (England) Regulations 2000 and the accompanying DETR Circular 02/2000.

This report provides technical information relevant to acid tar lagoons.

Within the Contaminated Land (England) Regulations 2000 this category of Special Site is defined as:

- *land which is contaminated land by reason of waste acid tars in, on or under the land. For the purposes of this definition, “waste acid tars” are tars which contain sulphuric acid, were produced as a result of the refining of benzole, used lubricants or petroleum and are or were stored on land used as a retention basin for the disposal of such tars.*

This report serves as a supplement to, and should be used in conjunction with, the following Environment Agency documents to provide supporting information relevant to the discharge of Environment Agency responsibilities for Special Sites:

- Part IIA EPA 1990 Process Documentation ; and
- DETR/Environment Agency. CLR11. Model Procedures for the Management of Contaminated Land (in preparation).

In addition, the reader is directed to other documents published by the Environment Agency, the DETR and others in the references and bibliography section of this report.

1.2 The Role of the Environment Agency in Relation to Special Sites

Full details of Environment Agency regulatory roles, responsibilities and procedures for dealing with Special Sites are provided in the Part IIA process documentation, and only a brief overview is included here.

The principal regulators for Part IIA (EPA 1990) are Local Authorities. The Environment Agency has an important complementary regulatory role with specific responsibilities including the provision of information and advice, and acting as enforcing authority in relation to Special Sites.

Local Authorities are responsible for identifying land in their areas which meets the statutory definition of contaminated land under Part IIA (EPA 1990). In doing so, Local Authorities will seek information from the Environment Agency, and advice in respect of pollution of controlled waters. Part IIA (EPA 1990) provides for certain land that meets the definition of

contaminated land to be designated as a Special Site, if it meets one of a number of categories of land prescribed in the Contaminated Land (England) Regulations 2000. In cases where a Local Authority believes that land, if found to be contaminated land, would subsequently be a Special Site, it will normally ask the Environment Agency to carry out a site inspection on its behalf, prior to determination of that land as contaminated land. However, the responsibility for formal determination of any land as contaminated land remains with the Local Authority in all cases.

Once land has been determined to be contaminated land, and where the Environment Agency and Local Authority agree (or the Secretary of State decides) that the land is also a Special Site, the Environment Agency will take over the role of enforcing authority from the Local Authority. Remediation of the site may include further investigation and assessment (assessment action), action to remedy the unacceptable risks identified (remedial treatment action) or monitoring (monitoring action). The Agency is responsible for maintaining a public register of regulatory action for Special Sites.

1.3 How to Use this Technical Guidance

This series of reports on Special Sites is primarily intended to provide Environment Agency Officers with the specialist technical information required when dealing with Special Sites under Part IIA (EPA 1990). Thus, every effort has been made to minimise the overlap with other guidance on generic aspects of contaminated land identification, assessment and management. In practice, it is likely that the reports will also prove useful to Local Authority officers, and others, when dealing with these types of sites.

The reports focus on the categories of land identified by Regulation 2 of the Contaminated Land (England) Regulations 2000. Separate guidance has been developed for those sites that are Special Sites by virtue of the seriousness of pollution of controlled waters (defined by Regulation 3 of the Contaminated Land (England) Regulations 2000).

The information contained in each report is arranged and presented so that it can easily be drawn upon when using other relevant guidance such as the Part IIA EPA 1990 process documentation. It begins with background information on, for example, the industrial process and facility description; further sections describe key issues that should be considered during the characterisation, evaluation, remediation and validation stages for each category of Special Site. References and a bibliography are also provided, together with a glossary of terms (both general contaminated land industry terms and also those specific to the individual technical field).

The format adopted in the report aims to assist the reader in the practical use of the technical information it contains by the inclusion of, where appropriate, selected checklists, diagrams, photographs, case studies and the highlighting of key technical information. In addition, at the start of each of the sections, a list of the key questions is included that highlight the issues covered by the section. The key issues that are addressed in the various sections of this report are as follows.

SECTION 2: INDUSTRIAL PROCESS/FACILITY DESCRIPTION

1. What is acid tar?
2. What are the main features of acid tar disposal sites?
3. How were acid tars managed?
4. What are the processes that produce acid tars and how do the acid tars differ?
5. What quantities of acid tars may be expected to be associated with each refining process?

SECTION 3: PHYSICAL AND CHEMICAL CHARACTERISTICS OF CONTAMINANTS

1. What are the chemical and physical characteristics of acid tars?
2. What classes of chemicals are found?
3. What typical concentrations of these chemicals could be expected?
4. What specific contaminants are found?
5. How do the main contaminants behave in the environment?

SECTION 4: SITE CHARACTERISATION

1. Which information sources should be used for the desk study?
2. How should the investigation be approached?
3. What are the main differences from a conventional contaminated land investigation?
4. Are special sampling and sample handling procedures required?
5. What should be analysed for and when?

SECTION 5: SITE EVALUATION

1. What are the primary pollutant linkages that should be assessed?
2. Which pollutant linkages are likely to be the most significant?
3. When is it appropriate/inappropriate to apply conventional risk assessment methods to this category of Special Sites?

SECTION 6: REMEDIATION ASPECTS

1. Which remediation technologies could be appropriate?
2. What are the main constraints and advantages to each of the applicable remediation technologies/engineering methods?
3. What are the anticipated perception/community impacts of the remediation technologies?
4. How can the remediation process be validated?

SECTION 7: HEALTH AND SAFETY

1. In what way are health and safety considerations influenced by the nature of acid tar lagoons?
2. What are the specific issues for selection of working methods?
3. What are the specific issues for selection of personal protective equipment?

1.4 Risk Communication Issues

Public awareness of contamination issues, together with the general perception of associated risks and the potential for harm (in the conventional sense) has increased during the 1980s and 1990s. Useful guidance with respect to risk communication issues can be found in Environment Agency R&D Technical Report P142 “Communicating Understanding of Contaminated Land Risks” (SNIFFER 1999).

1.5 Linkages Between the Guidance Reports and the Special Site Categories

Many of the Special Site categories are likely to include technical aspects that are incorporated into more than one of the seven individual guidance reports. A matrix showing the links that may be relevant between the guidance reports and the Special Site categories is given below in Table 1.1.

Table 1.1 - Linkage between guidance reports and Special Site categories

Special Sites Categories <i>(for full definitions see the Contaminated Land (England) Regulations 2000)</i>	Reports in This Series of Particular Relevance to Each Special Sites Category						
	<i>P5-042/TR/1 MOD Land</i>	<i>P5-042/TR/2 Chemical Weapons</i>	<i>P5-042/TR/3 Explosives Manufacturing</i>	<i>P5-042/TR/4 Acid Tar Lagoons</i>	<i>P5-042/TR/5 Petroleum Refineries</i>	<i>P5-042/TR/6 Nuclear Establishments</i>	<i>P5-042/TR/7 Prescribed Processes Designated for Central Control</i>
Regulation 3 Land	land to which Regulation 3 applies is dealt with separately from this series of reports						
Acid Tar Lagoons				√	√		
Petroleum Refineries				√	√		√
Explosives Manufacturing or Processing Sites	√	√	√			√	√
Prescribed Processes Designated for Central Control			√		√		√
Nuclear Licensed Sites	√	√	√			√	
Current Naval, Military and Air Force Land	√	√	√		√	√	
Chemical Sites	√	√	√				
AWE Sites	√		√			√	
S.30 of the Armed Forces Act Land	√		√			√	

2. INDUSTRIAL PROCESS/FACILITY DESCRIPTION

KEY QUESTIONS COVERED IN THIS SECTION

1. What is acid tar?
2. What are the main features of acid tar disposal sites?
3. How were acid tars managed?
4. What are the processes that produce acid tars and how do the acid tars differ?
5. What quantities of acid tars may be expected to be associated with each refining process?

2.1 Scope

This section presents a general overview of the key points relating to sites where acid tars may be encountered, the types of sites that may have contamination of this nature and their distribution and extent in the UK. It also provides a description of the main processes and activities that have occurred on sites where acid tars have been stored or disposed of in lagoons and which are likely to have resulted in ground contamination. Whilst acid tar lagoon sites can contain a range of contaminants (as a result of disposal of other wastes with the acid tar) the main contaminants of concern that will be dealt with in detail in this section, are those that are associated with acid tars themselves.

2.1.1 What constitutes acid tars

Tars are liquid or semi-solid residues of mixed chemical composition resulting from the carbonisation of organic materials in a high temperature thermal process. Acid tars are normally defined as tars of high sulphuric acid content and arise from the refining of oils by the addition of sulphuric acid, thereby containing sulphonated organic compounds.

The relevant definition of land required to be designated as a Special Site in the Contaminated Land (England) Regulations 2000 is

“land which is contaminated by reason of waste acid tars in, on or under the land”.

In these regulations, “waste acid tars” are defined as tars that:

- (a) contain sulphuric acid;
- (b) were produced as a result of the refining of benzole, used lubricants or petroleum; and
- (c) are or were stored on land used as a retention basin for the disposal of such tars”.

Acid tars should not be confused with tar acids. The latter are acidic compounds within tars such as phenol, cresols and xylenols which may be extracted by distillation and subsequently refined. Tars normally contain tar acids but tars are only termed *acid tars* where sulphuric acid has been added as part of a refining process.

2.1.2 Overview of acid tar lagoon sites

General points regarding acid tar lagoon sites include the following:

- acid tars have historically been generated as by-products of benzole refining, refining petroleum fractions (particularly white oil) and oil re-refining;
- the nature of the acid tars will depend to a degree on their origin. For example, acid tar arising from a specialist refinery processes involving the treatment of petroleum fractions with sulphuric acid may comprise black, tarry deposits. However, that from washing of benzole (BTX fractions) with sulphuric acid may be an odorous dark coloured liquid;
- acid tars have a very variable composition between sites and even within one lagoon, but are usually characterised by a weathered, crusty and relatively solid surface, with more fluid tars below;
- *in situ*, acid tar comprises a mass of hydrocarbons that is generally viscous and tarry with low pH. Layers of acid tar may be separated with intermittent soil layers or other deposited wastes;
- surrounding soils are likely to be contaminated to varying degrees with tars and hydrocarbons;
- some lagoons, in particular the older ones, are likely to have been filled with untreated tars. This was done either as a temporary measure to allow weathering to reduce the acidity, prior to disposal or incineration, or as the permanent disposal method. The more recently deposited lagoons may contain partially treated tars. Treatment may have been by the use of lime, in an attempt at neutralisation, or by igniting the tars *in situ*;
- attempts will usually have been made at covering or capping the tars, often with soil, sand, ash or domestic refuse. However, fluid tars can 'bleed' to the surface and solid capping material may sink into them. The tars that rise to the surface can expand and soften further in the sun and, potentially, may overflow resulting in movement off-site;
- some acid tar lagoons have also been used as disposal sites for other materials and it is not uncommon to find other wastes such as demolition materials and chemical drums in the lagoons.

2.1.3 Origins of acid tars

Acid tars have been generated historically in the UK as by-products of three distinct industrial processes (consistent with the definition of waste acid tars in the Contaminated Land (England) Regulations 2000):

- benzole refining;
- refining petroleum fractions, particularly in white oil production; and
- oil re-refining.

A brief outline of each of these processes is provided below.

Benzole Refining Process

- Benzole is a mixture of predominantly aromatic hydrocarbons that result from the washing of residues from coal carbonisation processes with concentrated sulphuric acid to remove impurities, followed by distillation;
- use of relatively untreated benzole in motor vehicle fuel declined in the 1960s and attempts were made at producing a more saleable product, including the use of more severe acid treatment that produced a more acidic, thicker, more complex acid tar than previously;
- attempts to find new markets for benzole failed, however, and there are now very few benzole refineries in existence.

White Oil Production Process

- White oil is a liquid paraffin, frequently used in medicinal preparation, that is produced by removing unsaturated and aromatic hydrocarbons together with sulphur compounds from heavy lubricant fractions;
- the process involved a repetitive series of acid and alkali treatments (the acid being 'oleum' - the most concentrated form of sulphuric acid) and the resulting acid tars were generally thicker, more acrid and more hazardous than those from benzole refining. Typically, Fuller's Earth was used to absorb residual acid and is generally found co-disposed with acid tars;
- sulphuric acid was also used in other petroleum fraction refining operations, particularly before 1930 when it was the only available process.

Oil Re-refining Process (including oil refining)

- Oil re-refining involved the removal of impurities such as lead, zinc and manganese from spent lubricating oils using concentrated sulphuric acid;
- the acid tar resulting from this process was much more variable in composition than that from benzole refining and white oil production; its composition being dependent on a number of variables including the nature of the oil, the contaminants it contained and the amount of acid used.

Overall Comments

Acid tars can be of very variable composition even from one type of process at one site. This is a function of variable process conditions and, in particular, the quantity and concentration of acid used. Thus tars in one part of a lagoon may differ markedly from those in other parts of the lagoon - especially in terms of pH. The tar composition and quantities produced depended on a number of variables including the type of coal/oil, carbonisation temperature (for benzole) and product required. Some generalisations can be made as set out in Box 2.1.

Box 2.1 Comments on differences between tars from different types of refining

- The thickest tars resulted from the use of small quantities of concentrated acids;
- the thinnest tars resulted from the use of large quantities of weak acids.

Benzole refining for motor benzole (pre-1960s)

The aim was to purify the aromatics (BTX) without sulphonating them significantly since the latter would lead to inadvertent removal of the wanted aromatics. Therefore since process conditions must not be too severe, a relatively weak acid was used and the resulting tars were relatively thin.

Purer benzole fractions (post-1960s)

A more severe acid treatment using more concentrated acids was required and the resulting tars were more viscous.

White oil production

Aromatics had to be removed which required 'oleum' (the most concentrated form of sulphuric acid) and the resultant tar was thicker, more acrid and more noxious than that generally arising from benzole refining.

Oil re-refining

The volume and composition of the acid tar depended on the extent and type of contamination in the original oil, the contact time with the acid used and the process efficiency. Therefore a wide range of acid tars was produced.

Acid tars that are produced currently in the UK are either incinerated or treated with alkalis prior to disposal in controlled landfill sites. In the past, producers frequently dumped them on-site (usually in a lagoon or void) in an uncontrolled manner. In some cases, this occurred over periods as long as 100 years, as various attempts to treat and utilise the tar were of relatively limited success.

2.2 Distribution and Extent of Acid Tar Lagoon Sites in the UK

2.2.1 Key points

The potential occurrence of acid tar lagoons is widespread because of the geographic extent of the industries that they are often found associated with. Large volumes of acid tar have been produced in the past, most of which would have been deposited in lagoons on-site at the point of manufacture, or in voids or on waste land close to the point of production.

2.2.2 Production process characteristics

Information on the location characteristics and production estimates for each production process are set out below.

Benzole Refining

- Historically, most benzole refining plants were located near coking works and larger coal gas manufacturing works ('gasworks');
- in the 1930s there were about 140 benzole refining plants;
- the total annual quantity of benzole refined peaked in the late 1950s (estimated 90,000 tonnes of acid tar produced annually) but at only around 50-60 plants;
- the number of plants then dropped sharply to less than ten in the 1970s (estimated 15,000 tonnes of acid tar produced annually);
- in 1982, only three benzole refining plants remained operational.

Box 2.2 Scenario: What quantity of acid tars might be found at a benzole refining site?

If we adopt the estimate of 2.5 million tonnes of acid tars produced in total, then this, divided by 140 sites, averages about 18,000 tonnes per site. In fact, this is distorted somewhat by a small number of large sites. For example, Port Clarence in Middlesbrough appears to have generated some 48,000 tonnes of acid tars between 1935 and 1955. Nevertheless, it gives an indication of the quantities.

As a 'rule of thumb', the quantity of acid tars produced is 10 per cent of the corresponding crude benzole production on a weight-for-weight basis.

White Oil

- Acid tar lagoons from white oil production generally follow the distribution of oil refineries in the UK which have typically been sited at coastal locations;
- figures for acid tar production from white oil refineries are often not available as the figures were generally incorporated into the overall figures for desulphurisation;
- estimates suggest that between 8,000 and 12,000 tonnes of acid tar were produced annually per refinery at the height of production in the 1950s at an estimated ten to twelve sites in the UK (annual total of around 100,000 tonnes of acid tar);
- over the period 1930 –1980, there could have been as much as 2 million tonnes of acid tar produced in total;
- in 1980 there were six refineries producing acid tars but by 1986 there was only one.

Box 2.3 Scenario: What quantity of acid tars might be found at a white oil refinery?

If we assume, based on the above, an average of 10,000 tonnes of acid tars produced per refinery per year, then a refinery operating over 40 years would have produced some 400,000 tonnes of acid tars.

A plant at Lviv in the Ukraine reportedly has 300,000 tonnes of acid tars that were disposed of over several decades (International Conference on Analysis & Utilisation of Oily Wastes, AUZO '96, 1996).

The former Sand Springs refinery in Texas, which operated from 1870-1940 and was classed as a Superfund site, was found to have 100,000 cubic yards (around 90,000 tonnes) of acid tar out of a total of 135,000 cubic yards of petroleum wastes in several earthen pits. Sulphuric acid had been used to treat raw crude oil to polymerise unstable compounds. (Grajczak, PE. Remediation of acid tar sludge at a Superfund site, Texas, 1995.)

Re-refining

- Information relating to historical re-refining sites in the UK is very limited;
- during the Second World War there were an estimated 30-40, mainly small, re-refining plants set up to supply lubricating oils to the military. As government subsidies were withdrawn and pollution control legislation was tightened, many re-refining works closed. By the mid-1980s only one re-refining plant remained in operation, producing 500 tonnes of acid tar per year;

- there are very few records relating to the locations or the methods of acid tar disposal used. It is believed, however, that even at the larger re-refining sites there was little or no treatment of acid tars prior to disposal (this being usually on-site or close to the plant);
- there may therefore be a number of sites as yet undiscovered, which could have acid tar lagoons present.

Box 2.4 Scenario: What quantity of acid tars might be found at an oil re-refining site?

If we assume, based on the above, that a refining plant produced typically 500 tonnes of acid tars per year then 40 years operation would correspond to 20,000 tonnes.

An acid tar disposal area for a re-refinery that was remediated in the 1990s cost approximately £1 million to address*. It involved excavation and re-deposition in a licensed landfill as special waste (presumably after mixing with other materials). This cost would be broadly consistent with the quantity of acid tars indicated above.

* further details confidential

2.2.3 Uncertainties and unidentified sites

A definitive list of the location of sites where acid tar has been deposited is not available and there may be unidentified sites. However, from the discussion above, acid tar lagoons are likely to occur at:

- about 140 former benzole refining sites near larger gasworks and at coke-making sites;
- about twelve major oil refineries (white oil production); and
- about 30-40, mainly small, oil re-refining plants.

2.3 Key Site Features

- Disposal of acid tars is likely to have occurred in the most convenient location on or near the site in the easiest manner for the site operators as possible;
- topography, proximity and availability often controlled the choice of locations for disposal sites;
- on large sites, such as major refineries, disposal may (particularly more recently) have been within an engineered repository but cruder disposal is likely to have been practised historically in most situations, especially on smaller sites.

Box 2.5 Scenario: Acid tar disposal lagoons

This scenario illustrates issues that have arisen in real cases but does not represent an actual single site.

It was estimated that around 20,000 tonnes of viscous acid tars generated at a former benzole-refining site in the 1960s had been disposed of within former gravel extraction pits near to the original works (approx. 1 ha). Various other materials were added, both to give stability and as part of general waste disposal and the pits were ultimately capped (with sand/soil) and then grassed.

The acid tars eventually “bled” to the surface leading to complaints about odours and other potential hazards followed by a fire that burned for a number of days.

One part of the lagoon became unstable following unrelated engineering works at an adjacent site on a lower level and the tars began migrating.

The council fenced off the area as a minimum, temporary, safety measure but was not obliged to clean up the site because it was privately owned. Remedial works were finally enforced via provisions in a lease. All of the acid tar was removed from the lagoons, the sides were lined with quicklime and the holes backfilled with limestone to ensure complete neutralisation of any acid tar remaining.

A number of options were considered for the acid tars that were removed which varied in cost and feasibility. The characteristics of the wastes had been determined via a large-scale investigation and these had shown that incineration did not seem practicable due to the high “debris content” of the acid tar. Some attempts were made to burn, experimentally, some of the acid tars at a nearby cement kiln but these proved unsuccessful. Eventually, a land-based method was chosen and the acid tars were transported to three separate landfill sites.

A site visit three years later found evidence of both weathered (dry brownish appearance) and recently emerged acid tars (characteristic bituminous appearance) at the surface some distance from the remediated areas. Further investigations showed that there was another acid tar lagoon that had not been found previously and this also had to be investigated and remediated.

Box 2.5 Scenario: Acid tar disposal lagoons (continued)

By this time, disposal to formal landfill sites was not practicable, due to the reluctance of waste disposal operators to accept acid tars and a corresponding increase in price per tonne by five times over the three years. The final method chosen involved *in situ* treatment using quicklime to neutralise the acid tars together with Fuller's Earth. After the tar and quicklime had reacted and settled down (releasing a considerable amount of heat and steam), the treated material was re-deposited in layers, compacted, covered with subsoil and landscaped.

This second, *in situ*, remedial exercise took six months, twice as long as that of three years previously where the wastes were taken away. The area where acid tar wastes remained became a recreation ground whereas the other remediated areas where the tars were removed and replaced with limestone were redeveloped for light industrial units. The remediation by quicklime appears to have been successful, although generally the method of dispersion by chemical reaction was considered preferable. Similar treatment methods at another site were less successful, and should therefore be subject to treatability trials.

The principal receptors of concern were:

- *human health* – associated mainly with the highly corrosive acidic conditions and also the physical hazard of fires and unstable ground;
- *groundwater and surface waters* – particularly from mobile oils and dissolved phase contaminants;
- *adjacent buildings and infrastructure* – due mainly to the instability of the lagoon, mobility of the tars that had broken through to the surface and fire.

3. CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE PRINCIPAL CONTAMINANTS

KEY QUESTIONS ANSWERED IN THIS SECTION

1. What are the chemical and physical characteristics of acid tars?
2. What classes of chemicals are found?
3. What typical concentrations of these chemicals could be expected?
4. What specific contaminants are found?
5. How do the main contaminants behave in the environment?

3.1 Scope

This section presents an overview of the characteristics of acid tars. It includes information relating to their chemical and physical form, toxicity and behaviour in the environment.

Key information on the physical properties of acid tars is given in section 3.2 whilst section 3.3 provides chemical characterisation. Comments are also made on breakdown products of acid tars and mobility of chemicals present within the environment. A list of the chemicals that are potentially present in acid tar lagoons is in Appendix B.

3.2 Physical Properties

3.2.1 Viscosity

Acid tar is thixotropic i.e. it is relatively solid, becoming more liquid when agitated. It has a relatively low density of approximately 1.3 tonnes/m³ (lower than soil) and the viscosity varies markedly with temperature, becoming less viscous and more free-flowing during the summer months as the tars warm. In such conditions, tars may ‘bleed’ and rise through covering materials above to spread laterally across the surface. Depth considerations are important; with the surface layers typically being weathered to leave a thick and crusty surface, whilst more liquid conditions exist at depth.

As discussed in Section 2, the viscosity of acid tars varies with the refining process that gave rise to them (white oil refining generally giving rise to thicker tars than benzole refining). Viscosity also varies with the specific process conditions such as contact time of acid with the oils being refined and so conditions may be highly heterogeneous within the same lagoon or disposal site.

3.2.2 pH

The pH of acid tars is variable and dependent on the following:

- type of process that generated the acid tar;
- the amount and strength of sulphuric acid used in the process; and
- the degree of pre-treatment prior to disposal.

White oil refining gives rise to the most acidic tars, being below pH 1. Benzole refining is less severe (as aromatics must not be sulphonated to any significant extent); re-refining is variable. However, pH values are frequently 2 or lower unless wastes have been pre-treated.

As mentioned previously, at some sites the tars may have been neutralised prior to disposal. At others there may have been steam stripping/washing to remove and recover some of the sulphuric acid (for ammonium sulphate manufacture). A further method involved use of solvent oil (creosote) to extract sulphuric acid. Typically, however, the tars will have been placed in lagoons to “weather”.

3.2.3 Colour

Tars from re-refining (containing some oils) are generally browner than those from white oil production and benzole refining, which are darker (essentially black) and thicker. Acid tars that are exposed at the ground surface will weather over time and may take on a dry, brownish appearance.

3.2.4 Odour

All acid tars are odorous. Re-refining tars are generally characterised by petroleum or "oily" odours, while the benzole tars are generally more sulphurous. Sulphurous odours tend to disappear with time as sulphur dioxide is released from the tars. Other sulphur-based compounds, including thiophenes and mercaptans, may volatilise from the lagoon surface and these can be odorous. Hydrogen sulphide may also be released at low levels. The weathering process results in little odour or air pollution from the lagoon, although investigation and remediation will disturb the lower layers and may give rise to acidic vapours and the release of more volatile hydrocarbons.

The general physical properties of the different types of acid tars are summarised in Table 3.1, although it should be noted that colour, odour and viscosity can vary markedly, even within the same lagoon.

Table 3.1 - General Physical Characteristics of the Different Acid Tars

Origin of Acid Tars	Viscosity*	pH	Colour*	Odour*
<i>Benzole refining</i>	thin to fairly viscous	pH 2 or lower	Generally black	more sulphurous than other acid tars although sulphurous gases are liberated over time
<i>White oil production</i>	very viscous	the most acidic tars, pH below 1	Generally black	petroleum or “oily”
<i>Oil re-refining</i>	variable	pH 2 or lower	Generally browner than the other acid tars	petroleum or “oily”

* Viscosity, colour and odour can vary markedly, even within the same lagoon. Disposal of other wastes may also influence these characteristics.

3.3 Chemical Properties

3.3.1 Compositions

The chemical characteristics of acid tars are very difficult to define for several reasons. Firstly, acid tar composition varies between different types (benzole refining, oil refining, re-refining) and no two batches of acid tars are ever identical due to process variations, operating temperatures, contact times, etc.

There are various ways of classifying the chemical composition of acid tars. At its simplest, Baruah (1995) indicate the following “typical average” composition for acid tars:

	% by weight
Free sulphuric acid	1.2
Hydrocarbons (oily and tarry matter)	50-63
Water content	27-28
Ash content	8-10

However, this would appear to relate to tars that have been treated, as other sources indicate much higher sulphuric acid concentrations (for example, 65% by weight for benzole refining, 35-60% for oil refining, 25-92% for white oil production and 10-11% for oil re-refining).

Illustrative compositions for acid tars from benzole refining and oil re-refining are presented in Table 3.2.

Table 3.2 - Illustrative Acid Tar Composition (all % wt)

<i>Benzole refining</i>	
Sulphuric acid	33
Sulphonic acids	3
Water	7
Benzole	30
Insoluble matter	<1
<i>Oil Re-refining</i>	
Water-soluble sulphuric acid	27
Ash	4
Water insoluble acids	2
Ash	8
Volatiles	0.8
Lube oils	16
Polymers	16
Other polar	2
Asphaltenes etc	24
Lead	2-10

3.3.2 Principal phases

An alternative way of describing acid tars is in terms of the principal phases. Sources of acid tars contamination can exist in three phases (see Nesbit (1995) and Topilnitskij (1996)):

- a free tar phase comprising high molecular weight asphaltenes and polar hydrocarbons together with a certain proportion of mid-distillate hydrocarbons;
- free oil;
- a sulphate-rich acidic aqueous phase.

A large number of substances are potentially present in acid tar lagoons, due to either the tar itself or other materials that have been dumped in them. Table B.1 (Appendix B) provides a listing of contaminants that have been detected in or around acid tar lagoons, although this list is by no means exhaustive.

The chemicals listed in Table B.1, can be grouped into several categories, as follows:

- aliphatic hydrocarbons;
- aromatic hydrocarbons;
- phenols;
- metals;
- organic acids;
- sulphonated hydrocarbons; and
- gases such as hydrogen sulphide, sulphur dioxide and methane.

However, the chemicals tend to form a dense mixture in which pure compound physico-chemical properties do not apply (due to matrix effects).

The identity of non-tar related chemicals can vary greatly, although polychlorinated biphenyls (PCBs) are a common additional contaminant (presumably co-disposal of oily wastes). Where the acid tar disposal area was located at the source of production, the other materials may be expected to be process or plant-related (other oils, demolition wastes, etc.). However, a wider range of wastes may be found where tars were disposed of at general tips. These may benefit the containment of the acid tars by providing a degree of retardation of soluble components due to absorption processes.

3.4 Breakdown Products

Some breakdown by natural biodegradation will occur and can result in production, among other compounds, of hydrogen sulphide, sulphur dioxide and methane. Generally, rates of biodegradation within the main disposal area will be limited by toxic effects on bacteria (from high concentrations of contaminants and low pH). However, at the edges, more microbial action is likely. Although weathering is likely to release sulphur dioxide and reduce acidity somewhat (release of sulphur dioxide (as “puffs”) is an issue for remediation), there appears to have been little study of other breakdown products. However the higher molecular weight polycyclic aromatic hydrocarbons (PAHs) are likely to be relatively resistant to degradation.

3.5 Mobile Compounds

The chemicals liable to migration in or associated with groundwater are principally those in the aqueous phase (phenols and derivatives, dissolved sulphuric acid, BTEX compounds, organic acids) and free oils. The high molecular weight asphaltenes (tarry substances) have a low solubility and remain relatively immobile. High acidity levels surrounding the lagoons will also tend to mobilise metals such as iron from naturally occurring mineral deposits.

4. SITE CHARACTERISATION

KEY QUESTIONS ANSWERED IN THIS SECTION

1. Which information sources should be used for the desk study?
2. How should the investigation be approached?
3. What are the main differences from a conventional contaminated land investigation?
4. Are special sampling and sample handling procedures required?
5. What should be analysed for, when and how?

4.1 Scope

This section provides information on the specific approach that should be followed when conducting desk studies and site investigations on land associated with acid tar lagoons. The overall procedures involved in characterising contamination on such sites have many aspects which are common to other types of contaminated land site. Consequently any such generic guidance is explicitly excluded from the scope of this section which relates solely to the particular issues which are exclusive to acid tar lagoons.

4.2 Desk Study

4.2.1 Key issues

Acid tar lagoons often show surface expression as a result of tars breaking through the ground surface – the classic blackened ground without vegetation. This will be less apparent if the site has been hard-surfaced or recently re-surfaced with gravel for example. A walk-over survey may allow the presence of tar to be identified and for an approximate area to be inferred. The ground surface is likely to be flat with surface expression related to the presence of overburden only.

It may also be possible to infer the extent of deposition from studying topography on old historical maps or aerial photographs, for example, by looking for former voids near acid tar producers that have been infilled.

4.2.2 Operational time periods

It may be possible to infer the likely size of an acid tar lagoon from knowledge of the production history of the refining site (see Section 2). For example, as a ‘rule of thumb’, the quantity of acid tars produced at a benzole refinery site is 10 per cent of the corresponding crude benzole production on a weight-for-weight basis. Section 2 also gives probable average quantities of tars for each type of refining process.

4.2.3 Common mistakes

It is possible that coal tars could be mistaken for acid tars, as both will tend to give rise to barren ground – the pH is the factor distinguishing acid tars. The mobility of acid tars and their propensity to flow upwards and laterally creates the potential for contamination of areas previously thought to be free of acid tars.

4.2.4 Desk study check-list for acid tar lagoons

<p>Have the following specialist information sources been approached?</p> <ul style="list-style-type: none">- Department of the Environment Industry Profile: Gas works, coke works and other coal carbonisation plants, 1995.- Department of the Environment Industry Profile: Oil refineries and bulk storage of crude oil and petroleum products. 1995.
<p>Have historic maps and aerial photographs been studied to identify the location of former voids that have been infilled?</p>
<p>Has the likely source of the acid tars, in particular the nature of the process, been established and any information on the production history and operational period of production?</p>
<p>Were any of the following features present on the site?:</p> <ul style="list-style-type: none">- black or dark brown staining, evidence of oozing tars or unvegetated areas;- weathered surface tars;- hollows/depressions;- clay/gravel/sand pits;- bunded areas;- odorous areas; and- areas of former fires. <p>If yes to any of the above has the extent of these been established?</p>

4.3 Site Inspection and Investigation

4.3.1 Site inspection

The site inspection visits should always be based on the maximum available information that can possibly be obtained from the desk study phase and an initial conceptual model of the site. Although this is also the case with other types of contaminated land it is particularly important when dealing with acid tar lagoon sites due to the explicit physical hazards that may be present. Site staff will need to be equipped with the relevant level of personal protective equipment (PPE) and trained accordingly (see Section 7 for health and safety aspects).

As noted above, it may be possible by site inspection to gain an impression of the extent of acid tar disposal from its surface expression. The aspects to look for include generally flat land (although this may have been modified by deposits of superficial wastes), absence of

vegetation, black or dark brown staining and, of course, any sign of oozing tars. A ranging rod or similar implement may allow the ground to be probed for evidence of soft ground and tars. As this is withdrawn, any free liquids/tarry deposits remaining on the end may be tested for pH using appropriate pH papers or detectors.

4.3.2 Site investigation

Approach to Site Investigations

In relation to acid tar lagoons, the following issues are of particular relevance when planning an investigation strategy:

- likelihood of contaminant migration away from the lagoons (e.g. into groundwater and surrounding soil);
- many sites will have few records of the composition or extent of lagoons, due to their age, which can be in excess of 100 years. In such cases, aerial photographs can be of particular benefit in determining their extent and location, as can local residents and former employees of the producing works. In some cases, satellite images may be available that reveal impacts on vegetation (usually requiring specialist interpretation);
- geophysical techniques may be useful in delineating both the extent of lagoons and also the nature and thickness of the capping layer;
- an investigation will need to take into account the presence of features that could allow migration of tars away from the lagoon e.g. old mine workings, conduits, drainage channels, solution features etc; and
- key pieces of information relevant to planning the study include the type of refining operation likely to have given rise to the waste, the period of filling, the origin and identity of fill materials (including any wastes) and any treatment that has been carried out.

A phased approach to site investigation in which exploratory sampling is followed by a more detailed study is appropriate for acid tar lagoons. However, exploratory sampling may not be needed in all cases (e.g. where the existence of a lagoon is obvious). In designing the sampling density and locations, it may be possible to restrict the number of samples on the grounds that it is known that the material is homogenous.

Some acid tar lagoons are quite heterogeneous. For example, investigation of an acid tar pit in Derbyshire found that *“fill products ranged from materials involved in the process of reprocessing used oils (tar product, fullers earth and free flowing lubricating oils) to foundry sand, mining spoil and household refuse.”*, (Nesbit *et al* 1995). In this case, during remedial stages, it may be practical to segregate and deal with the different wastes separately and thus greater quantification via a more intensive sampling regime may be warranted. Where there are only discrete pockets of non-acid tar wastes all of the wastes are likely, in practice, to be treated as special waste and the variability within the lagoon need not be quantified to the same degree.

Geophysical methods, such as resistivity surveys, ground penetrating radar (GPR) and shallow seismic surveys can be used to define the boundaries of lagoons, subject to certain limitations of each approach. The simplest technique is GPR, but this should be combined with a resistivity or seismic survey in order to improve confidence in the interpretation of the results.

When planning an investigation, careful consideration should be given to the possibility of off-site migration of contaminants in groundwater from the base of the lagoon, especially at older sites. Estimated contaminant travel times and contaminant flow direction should be used to assist in the planning of any groundwater survey.

The migration of liquid tar from acid tar lagoons is a possibility, although it is unlikely to have occurred in most cases. Old mine workings or conduits could, however, allow migration of tars as could fissured strata. Investigations of groundwater quality should be conducted with the possibility of migration in mind, with a selection of monitoring wells being screened across the water table (liquid tar or free phase hydrocarbons will tend to float on the groundwater).

Intrusive Works

With regard to the use of intrusive investigation techniques at acid tar lagoons, the following points are relevant:

- careful consideration should be given to the methods adopted for the site investigation, as the ground may not be strong enough to support conventional drilling/excavation equipment and it may be difficult to keep trial pits and, in some cases, boreholes open;
- if the lagoons are of high fluidity, then a pontoon or similar supportive equipment will be required in order to provide a safe working surface (note that the fluidity of acid tars can vary within one lagoon). Surface probing can often be conducted from a hydraulic platform;
- the depth of contamination may vary considerably and establishing the base of the lagoon, if this is required, may involve drilling through several non-tarry layers (consisting of, for example, on-site soils, Fuller's Earth and imported soil/wastes). Care must be taken to ensure that the true base of the tar has been reached and that there are not further deposits of tar beneath any soil layer (note also that the acid tar may have migrated up through the soil layer, leading to an intermediate soil layer within the lagoon);
- attention should be paid to ensuring that any investigation does not lead to contamination of the underlying groundwater by the acid tar or its components by breaching low permeability media;
- excavated wastes, both solid and liquid, must be disposed of appropriately; and
- ideally, site investigations should be carried out during winter months when the material is less fluid and the production of hazardous vapours is reduced.

The choice of investigation technique will depend on site-specific considerations. A number of techniques are suitable for acid tar lagoons, as follows:

- whilst increasingly sophisticated drilling techniques are being utilised in contaminated land investigation, the cable percussive (“shell and auger”) technique is usually adequate for acid tar lagoons. This technique enables reasonable depths to be achieved, both chemical and physical samples to be collected and facilitates the installation of gas and groundwater monitoring wells. Whilst the weight of the drilling rig may be less than some other types, it may still require specialist pontoon structures if the lagoon is unstable and, as with some other techniques, it cannot penetrate large lumps of concrete, steel or thick wood;
- dynamic probing can also be used, which uses either a continuous pneumatic system or a drop hammer to drive the probe. Depending upon the rate of penetration, an indication of the thickness and type of materials present can be determined. Samples for analysis can be collected using a hollow stem or split spoon attachment;
- trial pits and trial trench excavations allow greater inspection of the waste types, larger samples to be taken and can be extremely valuable in helping to determine the lateral extent of the wastes. However, it will usually be necessary to import clean cover material to cover over the larger “scar” that is left at the ground surface from trial pits compared to boreholes;
- window sampling can be carried out to obtain in-fill information between trench excavations although it should not be the sole method of investigation, as individual pockets of tar can be easily missed;
- rotary drilling techniques are unlikely to be effective in acid tar lagoons due to the physical characteristics of the acid tars themselves and the greater weight of the majority of rotary rigs;
- gas and groundwater monitoring wells can be installed with response zones both below and in the acid tar lagoon. However, great care must be taken with borehole design and construction techniques when penetrating through the base of a lagoon into natural ground to avoid driving down contamination and short-circuiting contamination migration routes;
- drilling and well construction materials that are resistant to aggressive ground conditions will be needed e.g. stainless steel equipment is preferable to mild steel as this latter type can be corroded by the acidity of the tars. Similarly, slotted pipe and casing should be of high density polyethylene (HDPE) for maximum chemical resistance.

Adequate time and appropriate facilities will be needed for the decontamination of equipment coated in tars. For example, steam cleaning of augers will be needed between locations and all equipment, including vehicle tyres, will need to be thoroughly cleaned before leaving the site at the end of each day. Depending on the cleaning equipment used, it may be necessary to have access to mains power and water close to the wash down point (the location of which also needs to be carefully chosen).

Investigation locations will need to be re-instated and clean cover material used to cover exposed wastes. On some sites, the surface topography might suggest that local superficial soils may be “borrowed” for this purpose. However, great care should be taken in this to avoid inadvertently digging through into underlying wastes and exacerbating problems. It is usually necessary to make sure that there is a supply of clean imported cover material from the very start of an investigation. Each location should be re-instated in turn as it is finished, rather than re-instatement carried out as a self-contained exercise after all locations are finished. This is particularly important where the site is not entirely secure from public access.

Sampling Techniques

Conventional sample collection procedures during intrusive works are relevant to sampling from acid tar lagoons, provided consideration is given to the potential for highly acidic conditions and the presence of free hydrocarbons and volatile organic compounds. Thus:

- sampling containers should comprise amber glass jars with PTFE seals as a minimum (plastic sampling pots are unsuitable); and
- once collected, the samples should be stored at a controlled temperature of between 2°C and 4°C and be delivered to the laboratory within 24 hours of collection.

The sampling of surrounding media, if performed, should also be conducted in the light of the likely contaminants (e.g.. low molecular weight hydrocarbons in air/groundwater and acids in groundwater).

Gases should be measured in boreholes using appropriate instruments. In some cases, it may be useful to collect Gresham samples for laboratory analysis. Note that aluminium Gresham tubes can absorb hydrogen sulphide and so should not be used where analysis for this gas is required.

Early consideration should be given to the methods of, and equipment needed for, the containment and disposal of contaminated purge-water.

4.4 Common Mistakes

Too much attention may be paid to the sampling of the solid tars themselves whereas it is likely to be the liquid tars, free oils and aqueous phase that are more environmentally significant.

4.5 Chemical Analysis

Note - this section should be read in conjunction with Section 3.3, which provides analytical information on acid tars.

4.5.1 Approach

- Acid tars are chemically extremely complex with many thousands of individual chemicals, most of which (the asphaltenes) have been characterised to a very limited extent. When deciding what to analyse for, it is important to have regard to the objectives of the analysis that is to be undertaken. For example, if the immediate hazard posed to human health is the only hazard that needs to be assessed, then characterisation in terms of pH, volatile organic compounds and gas evolution (sulphur dioxide, hydrogen sulphide, methane) may be all that is required;
- even very simple analysis can indicate the likely source of the acid tars e.g. BTX at relatively high concentrations (% levels) will indicate that the acid tars originate from benzole refining and that risks to groundwater may be higher than for other types of acid tars due to the mobility and toxicity of BTX compounds;
- very simple analysis can also reveal variability between different lagoons e.g. acid content can vary between 10 and 90 per cent, water content between 5 and 40 per cent and organics content from 15 to 70 per cent;
- a more sophisticated analytical approach may be needed in some cases. If an assessment is being made of risks to groundwater or surface water, greater emphasis will need to be placed on characterising the organic component. In particular, characterising liquid tars and free oils present is likely to be important. This is likely to include both analysis of samples of free phase hydrocarbons from within the lagoon but also free phase and dissolved components in groundwater or surface water outside the lagoon. The heavy end asphaltenes (high molecular weight viscous tars) may be of less interest in this context although this is subject to confirmation of the hydrogeological regime and the absence of preferential migration routes off-site such as fissures, mine-workings etc;
- if the purpose of the assessment is to evaluate potential remedial technologies, then characterising various layers within the lagoon will be important in assessing the practicality of handling and achieving intimate mixing in any neutralisation or “dispersing by chemical reaction” (DCR) process. Chemical analysis will also be useful in this context in assessing the degree of heterogeneity which any treatment process will need to be able to address;
- if the tars are to be characterised for waste disposal purposes, then the acceptance criteria at landfill must be taken into account when developing the analytical schedule.

4.5.2 Analytical techniques

Acid tars do pose specific analytical problems, as the highly sulphonated polar residues make chromatographic analysis difficult. Nesbit *et al* (1995) detail non-conventional analysis used to characterise the nature of the organic material, including:

- class separation by thin layer chromatography/flame ionisation detection to separate aromatic hydrocarbons, saturated hydrocarbons and tarry residues;

- gas chromatography by simulating fractional distillation to produce a boiling point distribution curve (which can be compared to a series of relevant standards); and
- thermogravimetric analysis (analyse percent weight loss as a function of temperature) to indicate the thermal behaviour of different waste materials.

The first and third of these are low cost screening-type methods. The above analysis allows the major phases of contamination to be identified. In the particular study, the phases found were:

- a free tar phase (high molecular weight asphaltenes and polar hydrocarbons plus some mid-distillate hydrocarbons);
- a free-flowing oil mainly comprising mid-distillate saturated hydrocarbons (up to 85% of the cyclohexane extract was present in this form); and
- an aqueous phase with very high sulphate concentrations (greater than 10% by weight) and very acidic (pH<1).

It is recommended that, prior to finalising an investigation strategy, discussions are held with several laboratories in the context of specific objectives. This is because certain methods are not generally available (e.g. thermogravimetric analysis).

Leaching tests are a useful method of assessing potential mobility; there are a range of such tests including one derived by the former National Rivers Authority (NRA 1994). Laboratories will normally be able to assist in deciding the most appropriate leaching test method.

4.5.3 Detection limits

Detection limits need to be appropriate to the circumstances. If groundwater or surface waters are being sampled, for example, detection limits need to be below relevant environmental standards to allow risks by the source-pathway-receptor model to be assessed properly. This can require methods such as GCMS scans. Nevertheless, screening methods can be a useful adjunct or preliminary tool. It is best practice to report estimates of total uncertainty with all laboratory data.

5. SITE EVALUATION

KEY QUESTIONS ANSWERED IN THIS SECTION

1. What are the primary pollutant linkages that should be assessed?
2. Which pollutant linkages are likely to be the most significant?
3. When is it appropriate/inappropriate to apply conventional risk assessment methods to this category of Special Sites?

5.1 Scope

This section is intended to supplement the relevant Model Procedures and associated guidance on risk estimation and risk evaluation. It highlights the particular issues relating to acid tar lagoons rather than describing the conventional aspects of site evaluation.

5.2 Pollutant Linkages

5.2.1 Human health

The principal documented concerns for acid tar lagoons relate to nuisance and to risks to human health and safety. These include:

- *physical hazards* associated with soft and unstable ground, which could lead to a person or piece of plant sinking into a tar lagoon if access or trespass is possible. It may seem fairly safe to walk on the surface of a lagoon but in places, remaining stationary for more than a few seconds may lead to a slow but gradual sinking into the surface. A surface crust can also give a false sense of stability but may suddenly give way;
- *chemical hazards* associated with contact with acid tar breakout. The acidity (pH<1) is the greatest concern which can give rise to severe corrosive effects (e.g. skin burns, even corrosion of unsuitable footwear). The hazard will generally be associated with clear visible evidence of tar breakout through the upper surface or a bund, although may not be recognised as such when it first occurs or is quite limited in extent. Low pH could also potentially lead to dissolution of carbonate rocks. Tars also represent a hazard to health due to their carcinogenicity;
- *odours* may indicate risk from hazardous vapours/gases to the health of flora and fauna, those visiting the site and neighbouring properties. Odours may also result in public complaints (risks may be perceived or actual). This is likely to be associated with fresh tar outbreak or “tar relaxation” where tars break through the surface crust. These will typically be tarry odours but depending on composition may be described as oily or sulphurous (sulphur dioxide and hydrogen sulphide);
- *fire hazards* may be present at some sites, perhaps especially those from benzole refining where BTX compounds will be present but also at other sites. Fires can sustain themselves for days, if not longer. Burning of acid tars in lagoons was sometimes practised in the past to improve stability.

5.2.2 Water environment

There is little evidence in the literature of investigation or assessment of groundwater contamination associated with acid tar lagoons and it appears that, in the past, the principal concerns leading to remedial action have been those documented above.

Acid tar lagoons clearly represent a risk to groundwater or surface water (depending on the site-specific context) and the previous imbalance probably reflects the high cost of addressing acid tar lagoons. This has meant that, by and large, action in the past has been taken when it has been forced as a result of a situation that is clearly unacceptable in public health terms and has justified expenditure which, in today's terms could be in the several million pounds range.

However, the assessment of acid tar lagoons in the future can be expected to place a high importance on assessment of risks to controlled waters. In most respects, the assessment of such risks would follow a conventional approach as documented in the Model Procedures. Thus, there is the possibility of past or future off-site migration both of dissolved contaminants (e.g. benzene) or free phase liquid tars and oils. However, there are a number of considerations specific to acid tar lagoons as follows:

- whether other wastes are known to have been co-disposed with the acid tars. This could include general demolition type waste for stability reasons, but can also include domestic refuse (absorptive capacity) and other industrial and chemical wastes. Clearly, account needs to be taken of all that is known from previous investigations and where these wastes are present in quantities and patterns likely to impact on remedial works, they will need to be characterised;
- reduced percolation of precipitation where there is a crusted, low permeability surface;
- effect of acidity on naturally occurring mineral deposits, leading to mobilisation of metals in strata or other wastes;
- effect of acidity on certain natural strata such as limestone and chalk (increasing solution features and enlarging fissures);
- interaction between acid tars and other substances present are especially important when estimating risks to the water environment from acid tar lagoons. These can act to reduce mobility, by preferentially binding the deposits, or enhancing it, due to co-solvency effects.

5.2.3 Ecological systems

The risks to flora and fauna from the contaminants in acid tar lagoons together with vapours and gases produced, are similar to many other contaminated land/landfill sites. The clear exception to this is the severely acidic conditions that exist, particularly where acid tars have “bled” to the surface and the effects on flora and fauna that come into contact. The actual ecological issues need to be assessed on a site specific basis.

5.2.4 Buildings

Acid tar lagoons are ordinarily not built upon due to inherent stability problems and it is most unlikely that an acid tar lagoon would be developed without addressing risks to buildings associated with the tars.

There may occasionally be a risk to buildings or infrastructure such as roads associated with a sudden release of acid tars down a slope where these are held back by fragile supporting banks, especially where these are made unstable by engineering works nearby.

As indicated previously, acid tar lagoons may emit methane, hydrogen sulphide and other gases as a result of naturally occurring degradation processes. However, explosive or flammable levels of the former are unlikely, due to the relatively small quantities involved, and, in any case, buildings are very unlikely to have been placed directly on top of a lagoon. The possibility of lateral migration of gases off-site should be considered especially where areas of hardstanding are present and there are nearby buildings.

5.2.5 Generic pollutant linkage matrices for acid tar lagoon sites

A variety of pollutant linkages may be identified on acid tar lagoons and examples are given below. These are meant only as an initial guide to the types of issues and are not intended to be a substitute for the site-specific assessment which will be required in practice. However they should provide an initial indication of the pollutant linkages which should be considered in the site-specific assessment.

Table 5.1 - Examples of Pollutant Linkages

Source/Hazard	Pathways/Receptors
<i>Acid tars exposed/near surface</i>	Trespassers/visitors to the site and fauna– skin contact, vapour inhalation, fire risk, risk of sinking into tars. Neighbours – odour and hazardous vapours/gases. Flora – unsuitable physical and chemical conditions, poisonous soil gases.
<i>Acid tars at depth (e.g. >1 m below surface)</i>	Groundwater/surface water depending on the hydrogeological and hydrological regimes.
<i>Instability</i>	Buildings/infrastructure/personnel downslope – migrating tars and liquids.

5.3 Assessment of Investigation Data

The assessment of investigation data is conventional in approach and reference should be made to the Model Procedures.

As pH values can be below the conventional scale (of 1 to 14), a comment on the definition and interpretation of pH is made in Box 5.1.

Box 5.1 What does a pH of below 1 mean?

pH is defined as the negative of the logarithm of the hydrogen ion activity.

$$\text{i.e. } \text{pH} = -\log_{10} [\text{H}^+]_a$$

A solution of pH 1 is thus ten times the acidity of a solution of pH 2 and a solution of pH 0 is ten times as acidic as a solution of pH 1. Although the pH scale in normal use runs from 1 to 14, from the above equation it is clear that concentrated solutions of acid can have negative pH values, i.e. the pH scale can extend through zero to negative values.

A 1 mole per litre solution of sulphuric acid corresponds to 98 g of H₂SO₄ in 1 litre (roughly 10% by weight) and has a pH of about -0.3 (minus 0.3). It can be seen that very concentrated sulphuric acid solutions (65% by weight in some acid tars) will have an even more negative pH (although the approximation that hydrogen ion activity equals hydrogen ion concentration breaks down in very concentrated solutions).

The pH values that may be found on acid tar contaminated sites are very much more acidic than those likely to be found on most other types of sites.

5.4 Site Evaluation Check-list

The purpose of the site evaluation is to review all the risk based information to decide whether the estimated risks are unacceptable, taking into account the nature/scale of the risks and any technical uncertainties.

A check-list is provided below summarising issues specific to acid tar lagoons that need to be considered alongside the Model Procedures.

Have the following specific considerations for acid tar lagoons been included in the site evaluation?
The physical risk to visitors/trespassers/contractors and whether this is adequately addressed, for example by fencing and warning signs.
The physical risk associated with topography, e.g. land slide with release of tars, potential for breach of a bund wall.
The chemical risk to visitors/trespassers/fauna and flora associated with the high acidity of acid tars and also toxicity considerations.
The potential for release of toxic gases (especially sulphur dioxide, but also hydrogen sulphide), vapours (especially BTEX compounds) and dusts, and the associated inhalation risks.
Factors that influence the risk to controlled waters, including solubility of tars, mobility of free phase oils and tars and degradation potential in the unsaturated zone and in polluted groundwater.
The fire risk (including starting of a fire by trespassers/visitors) and build up of potentially explosive concentrations of flammable gases in buildings.
The uncertainties associated with variability within the lagoon and also any wastes of quite different origin that may have been disposed of with the acid tars.
The potential for gas generation and migration (taking account also of any co-disposal of domestic wastes).
Effect of pH on the environmental behaviour of contaminants (e.g. increased metal mobility, interaction with natural minerals).

6. REMEDIATION ASPECTS

KEY QUESTIONS ANSWERED IN THIS SECTION

1. Which remediation technologies could be appropriate?
2. What are the main constraints and advantages to each of the applicable remediation technologies/engineering methods?
3. What are the anticipated perception/community impacts of the remediation technologies?
4. How can the remediation process be validated?

6.1 Scope

This section provides detail on the most applicable remediation technologies which are currently available (or are likely to be available in the near future) on a commercial scale within the UK. The intention of this section is to enable the reader to select a short list of appropriate remediation technologies and to highlight the key issues that will need to be considered in the remediation design. It does not provide detailed guidance on remediation design.

6.2 Principal Remediation Technologies

6.2.1 Civil engineering approaches

Cover Systems and Barriers

- The use of cover systems is generally not appropriate for acid tar lagoons as there is a tendency for most capping materials to move gradually downwards through the mass of tarry material, with the acid tar eventually replacing it at the surface;
- the downwards movement of capping materials and upwards movement of acid tars can also result in potential disturbance to vertical barriers installed as part of the capping system.

Encapsulation

- Various proprietary polymer-based and inorganic cement-based encapsulation techniques were attempted in the 1970s, but neither process appears to have proved successful in the long term;
- these techniques may be considerably more expensive than neutralisation and landfill.

Excavation and Disposal

- Acid tars and incorporated wastes that cannot be segregated easily will be deemed special wastes and will need to be dealt with and transported appropriately and disposed of at a suitably licensed facility;

- to ensure the safe disposal of acid tars, treatment or at least partial treatment will be required involving some form of neutralisation (discussed in Section 6.2.5).

6.2.2 Biological based technologies

- Biological based techniques involve various forms of *ex situ* bioremediation, such as biopiles, landfarming, slurry phase biotreatment, windrow turning and *in situ* processes, such as bioventing. These techniques do pose difficulties for acid tars, due to their acidity, high concentrations of organic compounds and problems with bio-availability;
- the use of bioremediation requires neutralisation (or at least raising the pH to 5) via an intimate mixing of the tar and a neutralisation agent such as calcium oxide or calcium carbonate. The mixing process can be prohibitively difficult to achieve (see 6.2.5, below);
- even where neutralisation is achieved, the issue of bio-availability remains. The contamination as a solid mass is difficult to degrade due to its very low surface area : volume ratio. In order for significant degradation to take place, it needs to be fully dispersed as a suspension of fine particulates within a medium supplied with sufficient oxygen and nutrients. Given the solid nature of the tar this is difficult to achieve, even using specialist plant and equipment. Nevertheless, where these constraints can be overcome, it is of interest as a sustainable technique.

6.2.3 Chemical based technologies

- The only potentially applicable chemical based technology is that involving surface amendments (e.g. organic matter or an alkali such as lime), and only for surface or shallow depth contamination (see Remedial Treatment Action Data Sheets, Environment Agency 2001);
- the key problem is ensuring a suitably intimate mixture of lime and tar, since even with specialist plant this is likely to be difficult to achieve *in situ* especially with a lagoon of acid tar present. In any case, very large quantities of calcium oxide (quicklime) or other alkali may be required. A more advanced method may be appropriate, however, such as *ex situ* treatment or the use of a proprietary approach such as “Dispersing by Chemical Reaction” (DCR). DCR and lime-based systems are discussed further in Section 6.2.5.

6.2.4 Physical based technologies

- Air sparging and soil vapour extraction are not applicable to acid tar lagoons due to the fact that most of the contamination will be of low volatility;
- various washing systems may be applicable to associated contaminated soil but will not address the explicit tar deposits.

6.2.5 Solidification and stabilisation based technologies

- Solidification and stabilisation based technologies include cement and pozzolan-based systems, vitrification-based systems and lime-based systems. Of these, the latter are most applicable and they can be broadly divided into conventional neutralisation processes and proprietary methods such as DCR. Other solidification processes may also be applicable.

Neutralisation Using Conventional Methods

- Neutralisation may be achieved by the application of quicklime (calcium oxide) directly with the tar *in situ*. This may be possible where the tar forms a shallow lagoon, although, as previously noted, there are likely to be significant problems in obtaining a suitably intimate mixture. Alternatively, the process may be carried out *ex situ*, either in layers or in specially designed plant. Due to the problems in achieving fully effective treatment, it should be viewed as partial in nature and undertaken mainly as an intermediate stage prior to landfilling;
- neutralisation processes have been carried out to varying degrees in the past. Tars are first mixed with soil to give a friable, crumbly texture suitable for the neutralisation process. Contaminated soils from the site can be used for this purpose, the proportions may be up to 50:50 soil to tar. Neutralisation involves mixing the tar-soil mixture with lime (up to 30% lime). The resulting neutralised tar can then be landfilled;
- this option is becoming increasingly difficult as there are fewer suitable landfill sites available that will accept the waste. In 1998 the costs of disposal by this method were generally in the order of £100 to £150/tonne for treatment and disposal;
- other end uses have been suggested in the literature, such as a binder for coal briquetting, as a solid fuel for industrial furnaces, or as a paving material for roads of low traffic density (see Baruah(1995)). Although these may be technically feasible, they may not be commercially attractive unless the volume of tar to be disposed of is very substantial or such a route already exists. Nevertheless, rising landfill costs have caused re-examination of the potential for developing commercial applications employing wastes in road construction;
- a method known as "Pseudo-landfill" has also been used in the past, the disposal of acid tar in a 'clay vault' filled with rubber tyres that help prevent migration. The tars were covered with water and left for a month to form three layers: 1) a top oily layer which was removed and recovered as boiler fuel; 2) a layer of dilute sulphuric acid which was also removed; and 3) the tar layer, which remained in the clay pit. The pit was banded by layers of quicklime to neutralise any tar that migrated, and covered with 2 m of domestic refuse. The process still leaves a layer of acid tar in a pit, and the material can still pose problems in terms of odour and subsurface migration issues. In the context of the EU Landfill Directive, such a method is less likely to be embraced in the future.

Dispersing by Chemical Reaction (DCR)

- This process works by using hydrophobic calcium oxide mixed with organic components. The non-aqueous components of the acid tars are selectively adsorbed within the calcium oxide, and the water content of the acid tar reacts with the calcium oxide to give fine powdered calcium hydroxide. The contaminant is thereby encapsulated within this system, being water repellent and leaching resistant;
- as for other neutralisation processes, DCR treatment can be applied with the material excavated and placed in layers, and the proprietary calcium oxide added using mechanical equipment. However, this could have a significant space requirement. Alternatively, direct addition may take place *in situ*, provided that the tars are suitably shallow. The resultant material can potentially be used as fill (subject to leaching tests) or for road construction;
- there are several technical limitations to the process, including uncertainties regarding its permanence and the leachability of the treated material;
- operational constraints could include the area required for treatment and requirements for control on emissions, together with significant health and safety issues raised by the exothermic nature of the reaction;
- the durability of DCR treatment is likely to be better than for stabilisation techniques based on cement. This is because, for DCR, the oils can be pre-distributed through the calcium oxide prior to effecting the hydration reaction, thereby eliminating oil as a liquid phase. The hydration reaction forms calcium hydroxide, which has a high specific surface area. The oil is adsorbed onto the hydroxide in molecular thickness and this is considered by some to be virtually irreversible short of dissolving the calcium hydroxide substrate (Grajczak (1995));
- in the above reference, mention is made of application of DCR to acid tars in Germany where the subsequent product was disposed in an unlined cell and with apparently no detectable contamination in groundwater some 15 years later;
- in contrast, approaches based on cementation normally aim to produce a monolith with oil held as liquid phase droplets within the cementitious matrix. In this case, the long-term integrity depends on that of the matrix.

Box 6.1 Example of Remediation of Acid Tar Sludge by DCR Treatment (Grajczak, 1995)

Acid tar sludge from the former Sinclair refinery site in Texas (a Superfund site) was treated by the DCR process using a specially commissioned transportable treatment unit handling 180 US tons/hour. 137,000 cubic yards of waste (about 100,000 cubic yards of which was classified as acid tar) was treated in total. The stabilised waste was then disposed of in a landfill constructed on site to legislative standards. The treatment technology initially specified was incineration unless it could be proven that a solidification technology would be as effective. As site characterisation showed that neutralisation would be required to reduce sulphur dioxide emissions, this prompted detailed study of solidification/stabilisation technologies as an alternative to incineration.

Most of the waste, particularly that deeper in the pits, was in the form of slow flowing, viscous tar. Bench scale trials were conducted by vendors against established treatment goals (expressed in terms of parameters such as compressive strength, liquid release, and leach testing). Following examination of these and evaluation of tenders, a tender based on the DCR process was selected. The treatment unit comprised a waste crusher/feed system, a reagent feed system, an emissions control system and two parallel treatment trains (hoppers, mixer, reaction chamber). Emission control was required as the initial reaction is exothermic and dust and VOCs needed to be captured and treated for a minimum of 30 minutes following waste-reagent mixing. This comprised a hydrostatic precipitator for dust, a packed spray tower and activated carbon for organic vapours.

The material produced was described as homogeneous, dry, free-flowing, easy to transport and readily compacted in the landfill. It is similar to natural clays but without the affinity for water. The period from conceptual engineering to start-up was 12 months and the treatment period was 13 months. The project was reported by the above author to have been concluded successfully.

Other Processes

- Other processes include several involving solidification, similar to those used for the solidification of sewage sludge;
- two processes have been piloted in Germany with some success, one of which produced a solid concrete-like material and another produced a powder. However, certain problems were encountered, most notably the need for large quantities of bulking material (580 kg were needed to solidify 25 kg of acid tar). This could lead to disposal problems due to the large amount of space required.

6.2.6 Thermal based systems

- Thermal based systems can be divided into those utilising thermal desorption and those which involve incineration;
- the nature of the contamination (i.e. the sheer mass of tar) generally means that, for practical purposes, incineration is the only viable thermal based option.

Incineration

- Incineration is an *ex situ* treatment that destroys the contaminants by thermal oxidation;
- the systems available for remediation include direct fired and indirectly fired incinerators, fluidised bed incinerators and infra red incinerators;
- acid tars are likely to require physical pre-treatment (drying) prior to incineration and the residue from the incineration process is likely to require appropriate disposal measures;
- incineration has been carried out in the past, and is currently the favoured option in the UK for treatment of acid tars from refinery processes, with 6,500 of the 8,000 tonnes produced annually in the UK being incinerated;
- there are a number of problems associated with this option, however, as follows:
 - wide variation in terms of properties of the tar leading to variation in the efficiency of incineration;
 - high sulphur content of the tar and the resulting need for scrubbers to remove sulphur dioxide from the waste stream;
 - presence of heavy metals, which have strict emission controls; and
 - presence of additional contaminants in the tar, including physical objects such as building materials (especially bricks) and drums, and neutralising materials such as lime.
- Cement kilns have considerable potential for acid tar incineration due to the long residence time and high temperatures together with their capacity for sulphur dioxide absorption. Whilst this technology has been successfully used for this purpose in Europe, in particular in Germany, incinerators/cement kilns are closely controlled under the Prescribed Process Regulations in the UK. An IPC authorisation (in due course a PPC consent) would have to be modified to allow acid tars to be disposed of at a particular facility. It is unlikely that a commercial incinerator facility would go to the extent of attempting to modify its authorisation unless a substantial volume of material was to be provided for disposal.

6.3 Natural Attenuation

Natural attenuation refers to the reduction of a contaminant concentration via naturally occurring physical, chemical or biological processes. For petroleum products, depending on specific site conditions, this can be an important factor in reducing contaminant concentrations, the most important processes being (i) biodegradation by micro-organisms naturally present in the soil and groundwater; (ii) weathering of surface spillages; and, (iii) volatilisation. Additional processes include retardation, sorption, hydrodynamic dispersion and dilution.

The main factors that dictate the rate of biodegradation are the oxygen supply (degradation is generally more rapid under aerobic conditions) and the molecular structure of the petroleum products. As described in TPHCWG (1998), the rate of biodegradation according to molecular structure is typically affected as follows:

- n-alkanes especially in the C10 – C25 range (e.g. diesel and gasoline) degrade more easily;
- isoalkanes degrade more slowly;
- alkenes degrade more slowly than alkanes;
- BTEX degradation occurs if they are in concentrations not toxic to the micro-organisms present;
- PAHs degrade more slowly than monoaromatics; and
- degradation of higher molecular weight cycloalkanes may be slower.

However, consideration should be given to those chemicals which degrade to more toxic daughter products.

Natural attenuation will not be applicable as a remediation option on all sites, and will only be acceptable if it can be demonstrated that the aforementioned processes are reducing the pollutant load such that there is no current or future unacceptable risk to receptors or are expected to do so over an acceptable timescale. A thorough site investigation and characterisation is required to understand the hydrogeology and geology of the site, and to determine whether these processes are active. In addition, natural attenuation will require on-going monitoring (not only of the pollutant, but also for example, oxygen, carbon dioxide and methane concentrations if biodegradation is occurring) until it can be demonstrated that there is no unacceptable risk to receptors.

The main benefits of natural attenuation are (i) treatment plants (and their associated costs) are not required; (ii) avoidance of utilisation of landfill capacity; and (iii) relatively little surface disturbance. The main disadvantages are (i) a long time periods and (ii) the need for continuous monitoring and a robust scientific argument. Further information can be obtained from the Model Procedures, Environment Agency R&D publication 95 (2000) and TPHCWG (1998).

The potential effectiveness of remediation by natural attenuation of petroleum hydrocarbons in groundwater arising from an acid tar lagoon will depend on the site-specific characteristics. Thus, for example, if the principal issue is dissolved benzene in groundwater then there is a greater *a priori* likelihood of significant natural attenuation than if the principal issue is free-phase oils.

Table 6.1 - Remedial Options/Techniques – Soils

Remedial Technology	Potential Effectiveness of Technology	Operational Requirements	Special Requirements	Permit	Social/Community Impact Issues	Information Requirements	Post Remediation Conditions		
							Short Term Validation	Long Term Monitoring	Other
Cover systems and barriers	Generally not effective due to movement of material within the lagoon					Long-term effectiveness of engineered barriers.	√	√	
Encapsulation	Limited evidence suggests unsuccessful					Durability of treated material.	√	√	
Excavation and disposal	Effective	Pre-treatment on site likely to be necessary to reduce acidity and emissions	Pre-treatment likely to require Waste Management (PPC) Licence. Liaison with local authority Environmental Health required.		Could be substantial if location is sensitive due to large numbers of vehicle movements, odour from excavation and movements	Characterisation of acid tars: acidity, propensity for sulphur dioxide emissions, free oil, other wastes present	√	√	
Biological-based processes	Difficult to achieve effectiveness for explicit tars due to the low pH, high tar concentrations and difficulty achieving the necessary mixing		Mobile plant waste management licence			Susceptibility of tars to biodegradation	√		
Physical-based technologies (air sparging, soil vapour extraction, soils washing)	Unlikely to be effective for the lagoon		Mobile plant waste management licence. Liaison with local authority Environmental Health on atmospheric releases		Emissions to air		√		

Table 6.1 - Remedial Options/Techniques – Soils (continued)

Remedial Technology	Potential Effectiveness of Technology	Operational Requirements	Special Requirements	Permit	Social/Community Impact Issues	Information Requirements	Post Remediation Conditions		
							Short Term Validation	Long Term Monitoring	Other
Chemical based technologies	DCR has been effective. More conventional neutralisation (lime) will provide some benefit but may not be as enduring as DCR	Need transportable treatment plant (see box under DCR)	Mobile plant waste management licence. Liaison with local authority Environmental Health required.		There is scope to reduce emissions by capturing and treating. Traffic impacts will depend on whether final disposal of treated material is on site or off-site	As for excavation and disposal, plus laboratory trials on the specific wastes to be treated to establish leachability, compressive strength, etc.	√	X (although on-site disposal will require longer-term groundwater monitoring)	
Thermal based systems	High temperature incineration is proven	Availability of commercial incinerator with appropriate IPC/IPPC authorisation. Cement kilns are also theoretically attractive due to the high residence times and the ability to absorb sulphur dioxide in the cement, although a single project would be unlikely to be attractive enough for IPC/IPPC licence implications to be addressed	In most cases, pre-treatment on site would be needed to reduce emissions of sulphur dioxide and probably to reduce water content. Waste management licence will be required May be IPC/IPPC process under certain circumstances		As for excavation and disposal	As for excavation and disposal. Any chlorinated wastes that had been co-disposed or PVC would be an issue regarding possible dioxin generation	√		

Table 6.2 - Remedial Options/Techniques - Groundwater

Remedial Technology	Potential Effectiveness of Technology	Operational Requirements	Special Permit Requirements	Social/Community Impact Issues	Information Requirements	Post Remediation Conditions		
						Short Term Validation	Long Term Monitoring	Other
Groundwater pump & treat	Effective for removal of free phase oils and pH adjustment. Can also be used for subsequent air-stripping of BTEX compounds. Can also be used for hydraulic containment of a plume	Conventional wells, pumps, blowers, etc. based on site-specific design	Abstraction licence. Discharge Consent Mobile plant waste management licence required although Environment Agency has an enforcement position in this regard	Unlikely to be major	Characterisation of groundwater, nature of free phase oils and dissolved hydrocarbons	√	√	
Soil vapour extraction or air sparging	Only for sites where the principal issue is BTEX (benzole) contamination as the technique is not appropriate for middle or heavy end oils. Ideally requires permeable, uniform geology	Conventional wells, pumps, blowers, etc. based on site-specific design. Treatment of emissions to air likely to be required	Mobile plant waste management licence required.	Unlikely to be major	Characterisation of groundwater, nature of free phase oils and dissolved hydrocarbons	√	√	

Table 6.2 - Remedial Options/Techniques – Groundwater (continued)

Remedial Technology	Potential Effectiveness of Technology	Operational Requirements	Special Permit Requirements	Social/Community Impact Issues	Information Requirements	Post Remediation Conditions		
						Short Term Validation	Long Term Monitoring	Other
Biosparging	Effective for dissolved hydrocarbons but not for free phase since could disperse the product. Can form a 'polishing system'. Slow release peroxides can form a passive system.	Usual wells, pumps, blowers, etc.	Mobile plant waste management licence	Modest	Hydrogeological characterisation with air sparge test and characterisation of nature of free phase and dissolved hydrocarbons	√	√	
Natural Attenuation	Effective for lighter ends of petroleum products. Dependent on hydrogeology of site.	Monitoring and sampling wells.			Hydrogeological characteristics and repeated monitoring. of contaminant plume.	√	√	

6.4 Validation

The principles of validation are the same for the remediation of acid tar sites as for other contaminated sites.

In the case of strategies involving the removal of the acid tars for off-site licensed disposal or incineration (whether after pre-treatment or not), there will be a need to verify that the removal exercise has met the agreed criteria. Normally, this will involve taking samples at the base and edges of any excavation to confirm the degree and extent of any residual contamination together with random sampling in other areas.

If groundwater is to be remediated (for example, if there are free oils) then the normal principles will apply. Thus groundwater monitoring will be required at appropriate locations around the acid tar lagoon. Monitoring will be necessary before, during and after remediation, until risks are properly managed and a statistically valid data-set has been obtained that demonstrates that the concentrations and trends are acceptable. If groundwater is not to be remediated (i.e. if the strategy is one of mass removal of the source) then groundwater monitoring post-removal over a similar (or longer) period will still be appropriate. This will be required in order to demonstrate the improvement in groundwater quality and, where relevant, to demonstrate that natural attenuation is occurring in accordance with predictions.

If the remedial strategy involves stabilisation techniques such as DCR then it will be necessary to demonstrate that the agreed performance criteria are met in the finished product. If the product is to be disposed of or re-used on site (subject to any necessary waste management licence) then consideration will be required of demonstrating longer-term performance. In the case of an engineered landfill, this would in any case be addressed through the waste management licensing procedure.

7. HEALTH AND SAFETY

KEY QUESTIONS ANSWERED IN THIS SECTION

1. In what way are health and safety considerations influenced by the nature of acid tar lagoons?
2. What are the specific issues for selection of working methods?
3. What are the specific issues for selection of personal protective equipment?

7.1 Scope

Health and safety considerations are a statutory obligation for work on all contaminated sites. Within this section only specific health and safety issues which relates to work on acid tar lagoon sites is included. General guidance on health and safety issues for work on contaminated sites can be found in HSE (1991); CIRIA (1996); Thomas Telford (1993); and BDA (1992).

7.2 Specialist Legislation

There is no specialist legislation other than that which applies to conventional contaminated land work.

7.3 Specialist Working Methods and Equipment

7.3.1 Working methods

With regard to acid tar lagoons, the following factors will be relevant in developing working methods:

- corrosive hazards from the acidity of the tars and associated soil and groundwater contamination. Fresh acid tar has a sulphuric acid content of 65 per cent by weight and, even in old acid tar lagoons the potential for highly acidic conditions should not be underestimated. Groundwater around a site in Derbyshire was found to have a pH less than 1, see Nesbit *et al* (1995);
- the possibility of acidic vapours being generated (depending on the acid content of the tars, acidic vapours may either be emitted *in situ* or when excavations are performed into the tar mass). Acid tar waste is frequently saturated with sulphur dioxide trapped in pores and this is easily released when the waste is disturbed. It can be released in sudden puffs during excavation, see Grajczak (1995). This may also be an off-site issue if, for example, houses are in close proximity;
- toxicity considerations from hydrocarbons and other substances; and
- stability issues dictate the need for particular control on access;

- all personnel should follow a decontamination process that should consist of, at a minimum, the removal of overalls and boots, and the washing of hands and face.

The relative importance of each of the above will depend to some extent on the kind of acid tar (e.g. whether there was pre-treatment to reduce acidity) and the age of the deposit. With regard to stability issues, the lagoon surface may be relatively solid, especially during winter, while in summer, warming of the tars will lead to softening and expansion, leading to a loss of bearing capacity and surface spreading. If there is sufficient local knowledge about a particular site (e.g. if it is known to have been covered and is now tracked over by various site vehicles) then it may be possible for staff to walk on the site surface. However, if there is limited/no local knowledge then sites must be considered unsafe and further information should be gathered to determine whether the site is safe to walk on.

Further practical risk management issues to consider when undertaking site works on acid tar lagoons include the following:

- access to the lagoons themselves should be restricted to prevent personnel from walking across the site and limited to those working on the site.

7.3.2 Equipment

- PPE should be worn at all times to protect the skin from acid burns and contact with hydrocarbons and heavy metals. In many cases the pH may be 2 or lower and in some case below pH 1. Protective equipment should include acid resistant boots together with disposable overalls and gloves as a minimum. On some sites the tars may be of a more hazardous nature requiring the use of gloves, boots, overalls etc. made of chemical resistant (as well as acid resistant) materials (e.g. chlorinated polyethylene, viton, neoprene or PVC);
- eye protection should also be worn. Where vapours are not a problem safety goggles may be sufficient. Full face masks may need to be worn dependent on the results of vapour monitoring. Of particular concern are acidic vapours, also hydrogen sulphide and sulphur dioxide as well as lighter hydrocarbons which may be present within the tar.

As indicated previously, Table B.1 in Appendix B provides a list of contaminants that could be present within acid tar lagoons and this can be used in health and safety planning.

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APPENDIX B Table B.1 Chemicals Potentially Present in Acid Tar Lagoons

1,1,1-Trichloroethane	Cadmium	Naphthalene
1,1,2-Trichloro-1-propene	Carbon disulphide	Nickel
1,1,Thiobismethane	Chloroform	Nonane
1,4-Dichlorobenzene	Chloromethane	Octane
1-Cyclohexen-1-ol	Chromium	o-Xylene
1-Methyl-2-propolidimone	Chrysene	p-chloro-m-cresol
1-Methylcyclohexane	Cobalt	Pentamethylbenzene
1-Methylthiobutane	Copper	Phenanthrene
1-Methylthiopropene	Cyclohexane	Phenol
2,3,Dimethyl-2,5-cyclohexadiene-1,4-dione	Decane	Polychlorinated biphenyls
2,4,6-Trichlorophenol	Dibenzo(a,h)anthracene	Anthracene
2-Azodi-2,3,3-trimethylbutane	Diethyl disulphide	Potassium
2-Butanone	Diethylphthalate	Propane
2-Cyclohexen-1-one	Dimethyl sulphide	Propylbenzene
2-Hexanone	Dimethylbenzene	Propylene
2-methyl-2-butanol	Dimethylcyclohexane	p-Xylene
2-Methyl-2-propanol	Dimethylcyclopropane	Pyrene
2-Methylnaphthalene	Dimethylhexane	Selenium
2-Methylphenol	Dimethylpentane	Silver
2-Methylthiobutane	Dimethylthiocyclohexane	Sodium
3-Methylthiophene	Di-n-butylphthalate	Sulphate
4-Chloro-trans-hexanol	Di-n-octylphthalate	Sulphur dioxide
4-Methylphenol	Esters	Sulphuric acid
4-Nitrophenol	Ethane	Sulphurous acid
Acenaphthene	Ethene	Tetraethylester diphosphoric acid
Acenaphthylene	Ethylbenzene	Tetrahydro-2-methyl-2-thiopyrane
Acetone	Ethylhexane	Tetrahydro-2-methylthiophene
Acetylene	Ethylmethylbenzene	Tetrahydro-3-methylthiophene
Aluminium	Fluoranthene	Tetrahydrodimethylthiophene
Arsenic	Fluorene	Tetrahydrothiophene
Barium	Heptane	Tetramethylbenzene
Benzene	Hexane	Tetramethylcyclohexane
Benzo(a)anthracene	Iron	Thallium
Benzo(a)pyrene	Isobutane	Thiophene
Benzo(b)fluoranthene	Isopentane	Toluene
Benzo(g,h,i)perylene	Lead	Trimethylbenzene
Benzo(k)fluoranthene	Magnesium	Trimethylcyclohexane
Benzoic acid	Manganese	Trimethylcyclopropane
Beryllium	Mercury	Trimethylhexane
Bis(2-ethylhexyl)phthalate	Methane thiol	Trimethylpentane
Butadiene	Methylcyclohexane	Vanadium
Butane	Methylcyclopentane	Zinc
Butene	Methylheptane	
Butylbenzene phthalate	Methylhexanes	
C3-benzene,C4-benzene,C5-Benzene	Methylmercaptan	
C3-cyclohexane	Methylpentanes	
	Methylthiocyclohexane	
	m-Xylene	