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SUB 7

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subr:im bulletin

CL:AIRE's SUBR:IM bulletins present practical outcomes of research by the SUBR:IM consortium which have direct application to the brownfield and contaminated land communities. This bulletin provides a state of the art update on the science, assessment and remediation of acid tar lagoons.

Acid Tar Lagoons

1. INTRODUCTION

Acid tars are a unique and challenging waste product arising from petroleum refining processes which are now largely obsolete. Typically disposal routes were into existing holes in the ground to form lagoons up to several hectares in area and this legacy remains in many parts of the UK and worldwide.

Until recently there has been little research into acid tars and their environmental impact. This bulletin aims to partly address this information gap by providing a State of the Art update on the science, assessment and remediation of Acid Tar lagoons. Such issues have been previously covered in part by an Environment Agency R&D Technical Report (Nancarrow *et al.*, 2001). It is not the intention of this bulletin to duplicate such information where still valid, but to provide key updates, coupled with references to more detailed information. Also highlighted are current deficiencies in our knowledge.

The content of this bulletin is based on research carried out by the University of Sheffield and GMGU (Urban Vision Partnership Ltd) from 2003-2007 and was funded by the Engineering and Physical Sciences Research Council (EPSRC), with additional funding from the Environment Agency, as part of the SUBR:IM (Sustainable Urban Brownfield Regeneration: Integrated Management) consortium research project. It also draws on experience from two recent remediation projects carried out in Europe (Fig.1).

2. BACKGROUND TO ACID TAR LAGOONS

Acid tars are a waste residue of petrochemical processes, which are now mostly abandoned. Their production can be traced from the end of the 19th century (Milne *et al.*, 1986). Nancarrow *et al.* (2001) define acid tars as follows:

> "*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 sulfuric acid content and arise from the refining of oils by the addition of sulfuric acid, thereby containing sulfonated organic compounds*[1]."

There are three main processes that produce acid tars: benzole refining, white oil production and oil re-refining. Nancarrow *et al.* (2001) discuss these processes in detail and provide estimates of the historical UK production. The range of production processes and variations within these processes means that disposed tars can vary significantly from site to site and even within one site. Tar consistency can vary from thin/oily tars to highly viscous semi-solid tars. The thickest tars resulted from the use of small quantities of concentrated acids, while the thinnest tars tended to result from the use of large quantities of weak acids (Nancarrow *et al.*, 2001).

Historically, the methods used for acid tar disposal were mostly by landfill into existing holes or lined lagoons, usually near the former chemical plants. Typical lagoon depths reported in the literature for the UK vary from 4-10 m for open lagoons, and volumes vary from ~3,000-60,000 m^3 (Nichol, 2000; Chambers, 2001; Banks *et al.*, 1998). The tar sometimes underwent a limited pre-treatment, such as mixing with lime, though complete mixing was often difficult to achieve. Additionally, the white oil production process often involved use of Fuller's Earth to absorb residual acid and this is generally found co-disposed with these acid tars.

Figure 1: Acid tar lagoon, Rieme, Belgium.

At many sites, the opportunity was taken to dispose of other materials with the acid tars. These have included materials such as drums of various chemicals, sugar waste, sand, ash, clinker, vegetation, polychlorinated biphenyls (PCBs) etc. At these sites there is thus the combined challenge of handling the tars and the co-disposed materials.

Historically, remediation attempts have included treatment with lime and replacement, excavation and disposal to landfill (with or without treatment) and un-engineered capping. Capping is typically only partially successful and often results in acid tars 'bleeding' to the surface. This has been observed at many sites. Fire has also occurred at least once on an uncapped lagoon site (Reynolds, 2002).

3. PHYSICAL AND CHEMICAL CHARACTERISTICS OF ACID TARS

3.1 Physical Properties

3.1.1 Density

The density of acid tars has been reported at between 1020 and 1430 kg/m^3 (Hao and Smith, 2005) i.e. denser than water. High acid tar density relative to other (non-acid) tars is attributed in part to the often high content of denser sulfuric acid (density 1960 kg/m^3).

3.1.2 Viscosity

Acid tars are typically thixotropic (i.e. displaying a reduction in viscosity on agitation). Although there is no viscosity data in the literature for acid tars in the normal environmental temperature range, Hao and Smith (2005) estimate a

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[1] note spelling of sulphuric and sulphonated amended to be consistent with rest of document

factor of 10 change in viscosity between -10ºC and +20ºC for acid tars reported by Frolov *et al.* (1980). Seasonal temperature variation can thus result in significant changes in tar mobility from winter to summer.

3.1.3 Solubility

Physically acid tars can flow under gravity on the surface as a single phase and tar 'flow streams' have been observed to continue apparently unaltered into water bodies on lagoon sites. It is tempting to regard an acid tar as a dense non-aqueous phase liquid (DNAPL). However, leaching tests using water indicate that tar can undergo physical breakdown, with a portion of the tar going into solution or fine suspension, and residual tar remaining as insoluble fragments (Hao, 2008). The partial solubility of acid tars is attributed in part to the presence of sulfonic acids and other polar sulfur containing compounds which have surfactant like properties. The observed 'flow streams' are indicative of continued flow of tar that is being slowly leached. The chemicals liable to leaching/loss include: phenols and derivatives, dissolved sulfuric acid, BTEX compounds, organic acids and free oils (Nancarrow *et al.*, 2001; Hao, 2008).

3.1.4 Gas and vapour content

Acid tars can release significant quantities of sulfur dioxide when exposed to the air. This can be one of the main challenges involved when considering remediation of an acid tar lagoon. At present it is unclear as to what form the sulfur dioxide is present in acid tar and the mechanism of its release. Hao (2008) suggests that acid tar contains significant quantities of metastable sulfonic acids (RSO_3H, where R is used to represent any organic group). On disturbance or temperature increase these can decompose to release sulfur dioxide as follows:

2R-S(=O)(=O)-OH ---> R-S(=O)(=O)-O-R + H_2O + SO_2

(decomposition of sulfonic acid, releasing sulfonic ester, water and sulfur dioxide)

When heated, the sulfuric acid can also be decomposed and release sulfur dioxide:

R-H + R'-H + H_2SO_4 (heated) ---> R-R' + $2H_2O$ + SO_2

(thermal reduction of sulfuric acid in acid tars, releasing sulfur dioxide, water and polymeric hydrocarbon)

Loss of SO_2 and H_2O to, for example, the atmosphere, will tend to drive these reactions to the right hand side, thus explaining the enhancement of the process by disturbance.

Pensaert (2005) reports results of experiments to determine emissions from three different acid tars derived from an acid tar lagoon in Belgium. A controllable flow of pure air was blown over a known volume (with known exposed surface) of acid tar, and the outlet air was chemically analysed for any compound of interest. By varying the air flow and the temperature of the air and tars, it was investigated whether wind speed and seasonal conditions would influence the emission of volatile compounds from the tars.

The results indicated that:

- SO_2 was the main compound evaporating from the tars. H_2S was not released while only a minor amount of volatile organic compounds (VOCs) were released.
- The emission of SO_2 was not significantly influenced by a change in temperature in the range 5 to 35°C.
- The emission flux (g SO_2 per hour and per m^2 of exposed surface) was independent of the wind speed. The average SO_2 fluxes from the different types of tar at rest are: (i) liquid tars: 1 g/(m^2.h), (ii) viscous tars: 12 g/(m^2.h), (iii) solid tars: 500 g/(m^2.h)
- The emission fluxes increase by about 5 times when the tars are continuously disturbed.

The flux independence with wind speed indicates that outward diffusion of SO_2 within the tars is determining the emission kinetics. This will also result in the increased emission fluxes on disturbance.

3.2 Chemistry

3.2.1 Composition

Acid tar is a complex mixture of hydrocarbons, sulfuric acid, water and a varied range of co-disposed materials. The chemicals inside acid tar may contain compounds from the following categories: aliphatic hydrocarbons, aromatic hydrocarbons, phenols, metals, organic acids, sulfonated hydrocarbons and gases such as hydrogen sulfide, sulfur dioxide and methane (Nancarrow *et al.* 2001). Nancarrow *et al.* also provide an extensive list of chemicals that have been detected in or around acid tar lagoons.

3.2.2 pH

Nancarrow *et al.* (2001), report that typical acid tar pH levels are less than 2 and can fall below pH 1 for tars arising from white oil production. Pretreated tars will tend to have higher pH levels. Titration tests carried out on leachate and residue from acid tar samples (Hao, 2008) indicate a response indicative of a complex buffering system (see Fig. 2) with a slow rise in pH with titration by NaOH. It is inferred that the leachate contains a large range of acid species, most likely organic acids such as sulfonated acids, and chemically active solid surfaces affecting system chemical equilibrium.

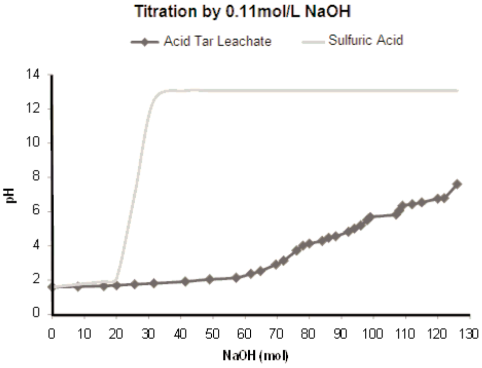

Figure 2: Example titration results on an acid tar leachate from Solid:Liquid 1:10 batch leaching test. Grey line is the theoretical titration curve for pure sulfuric acid and sodium hydroxide. The tar sample used was produced from an oil re-refining process.

The low pH introduced by the presence of acid tars can dissolve and mobilise metal species from the original environment or from co-disposed materials. Additionally there is anecdotal evidence that significant quantities of other gases may be produced such as CO_2 from e.g. reactions with carbonates in the ground.

3.2.3 Sulfur chemistry of acid tars

The sulfur chemistry of acid tars is extremely complicated and is not fully understood. The major sulfur compounds that may be present in acid tars are sulfur dioxide, sulfuric acid, sulfates, sulfonic acid and other organosulfur compounds contained by the crude material.

Sulfuric acid is an enormously important industrial chemical and it is used in organic refining industries as a high polarity solvent that can remove impurities (sulfur containing organics and unsaturated hydrocarbons) in organic mixtures such as crude benzole, lubricant oil and white oil that generate acid tars. Sulfuric acid is a strong mineral acid. It is soluble in water at all concentrations. Although nearly 100% sulfuric acid can be made, this loses SO_3 ($H_2SO_4 \rightleftharpoons H_2O + SO_3$) at the boiling point to produce 98.3% acid. The 98% grade is more stable in storage, and is the usual form of what is described as concentrated sulfuric acid, which is used in acid tar production.

The sulfuric acid is involved in many inorganic and organic processes which contribute to the unique behaviors of acid tars. There are various reagents within concentrated sulfuric acid, e.g. SO_3, HSO_4^-, H_2SO_4 etc, which are highly reactive and can generate complicated products under different conditions. In the production of acid tars, sulfonation is the major reaction that removes unsaturated hydrocarbons from the organic mixture while sulfur containing organic compounds are dissolved in concentrated sulfuric acid because of their higher polarity.

$R{=}R' + H_2SO_4 \dashrightarrow R{-}R'{-}S({=}O)({=}O){-}OH + H_2O$ (sulfonation)

This reaction is reversible but can be driven to completion by several techniques, e.g. removal of the water generated. The sulfonic acids may then in turn decompose to give off SO_2 as described in Section 3.1.4. This may explain the higher emission flux of the more solid tars. Apart from sulfuric acid, sulfonic acids are the most dominant acid within acid tars and contain highly variable species depending on the starting material and production conditions.

4. BIOLOGICAL ASPECTS

Some acid tar lagoon sites seem devoid of life, others have an often surprising amount of biological activity present around the site perimeter. Site observations imply that the biological activity is confined to plant and microbial life and primarily arises due to the presence of organic matter build up (such as leaf litter) on or around the lagoon. The implication is that the tar itself is not significantly toxic to organisms but modifies the local environment to favour certain types of organism. Primarily the modification is to a low pH environment favouring acidophiles. Acid-loving plant species (such as birch) have been observed growing around the perimeter and on small 'islands' on the surface of acid tar lagoons (Fig. 3). Additionally large biofilm colonies of extremophile algae have been found growing within the surface water of pH <2 overlying an acid tar lagoon. At present there are no reports in the literature of biological activity within the tar body itself.

Figure 3: Abundant plantlife on 'islands' on an acid tar lagoon with ponded water on its surface. The lagoon top water is contaminated by sulfuric acids, soluble, suspended and separate phase organic compounds. Note black deposits of organic particles around shoreline. Large biofilms of algae lie beneath the water surface.

The implication to be drawn from this is that there is potential for using biological treatment to deal with leachate and surface water overflow without toxicity concerns. However the scope to biodegrade the bulk tar itself is unknown.

Nevertheless the tar can kill plant life simply through physical smothering. This is observed where tar is slowly bleeding to the surface and flowing over the ground (Fig. 4). Additionally, where the surface of the main tar body remains fluid or viscous, it is difficult for soil bodies to build up without slowly sinking into the tar.

5. WEATHERING AND LEACHING CHARACTERISTICS

5.1 Weathering

Depending on environmental conditions, tar will weather into a range of forms (Hao, 2008). The most common form is a friable weathered tar (Fig. 5) typically observed on thin or isolated bodies of tar which are able to lose their water and organic volatile compounds content without being replenished from the bulk tar mass. This form of tar can produce dust-sized particles that are vulnerable to windblow and thus offsite migration.

Figure 4: Tar that has bled through the subsurface and is slowly flowing over grass.

Figure 5: Friable weathered tar arising from weathering of thin surface flows.

5.2 Leaching: Batch and Cascade Tests

When exposed to water, acid tar in all its forms, either original or weathered can leach significant quantities of sulfuric acid, and total organic carbon (TOC). Hao (2008) reports cascade tests up to 1:50 dilution that were still leaching significant quantities of total organic carbon, though the sulfate leaching was nearly exhausted at this stage. An example of the results is given in Figure 6.

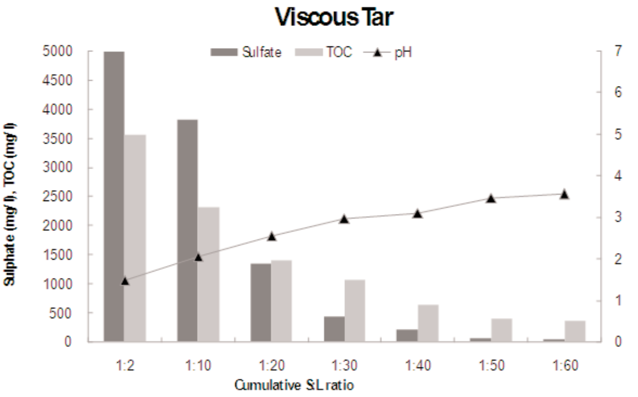

Figure 6: Leaching of sulfate, TOC and pH during cascade tests on a viscous tar arising from tar refining.

These tests were undertaken on a tar derived from oil re-refining. However other authors have found contrasting results. Nichol (2000) reports virtually no noteworthy transfer of contaminants from tar to any contacting water in laboratory leaching tests. Available field evidence in the literature also indicates no significant off-site migration of contaminants in ground or surface waters (Nichol, 2000; Banks *et al.* 1998). This may be due to a combination of low leaching and natural attenuation, however it may also only be specific to these particular lagoons and should not at present be generalised. Banks *et al.* (1998)

did however indicate that contamination from tar pits does have the effect of lowering the local groundwater pH and increasing concentration of chloride, sulfate and some metals (detailed organic analyses were not reported).

5.3 Leaching: Flow Cell Tests

Flow cell tests on a tar reported by Hao (2008) illustrate potential subsurface behaviour of tar when located on permeable strata (modelled as glass beads). Note that these results are based on tar samples derived from oil re-refining and may differ for other acid tar types. The key observation (Fig. 7) is that while tar produces a plume of soluble/finely suspended inorganic and organic components, it also is able to migrate in bulk in a manner reminiscent of a DNAPL. Since the tar is partially soluble, the bulk ‘fingers’ of migration provide greater area for leaching, and eventually leave a residual component of insoluble tar particles (Fig. 8).

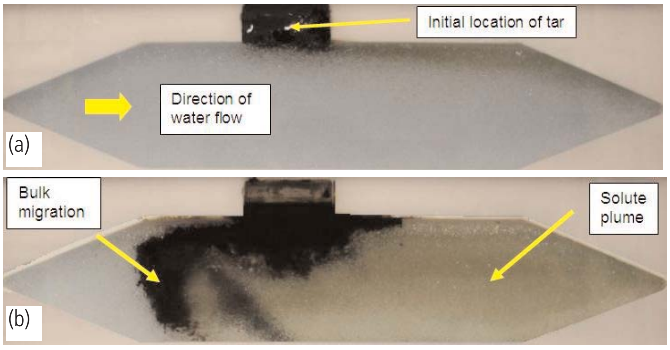

Figure 7: Flow cell test (a) initial leaching of soluble components only (b) bulk migration enhances leachable area.

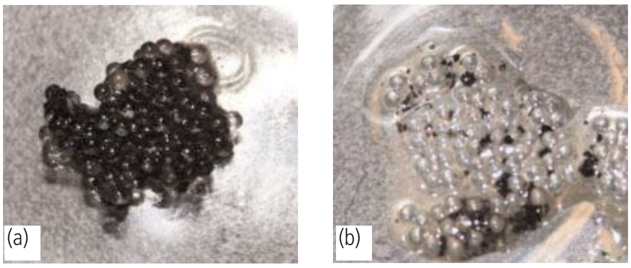

Figure 8: Residual tar particles following migration and leaching in a flow cell test (a) *in situ* state following test (b) flushing with water reveals residual particles of tar.

The observed behaviour indicates that acid tar might behave as a colloidal system (like bitumen) in which micelles of high molecular weight organics are dispersed in a mixed organic-water phase, and in which the organic and water phases are held together by the surfactant properties of the sulfonic acids.

6. ENVIRONMENTAL INTERACTION

6.1 Physical and Chemical Mobility of Acid Tar

In any consideration of the environmental impact of an acid tar lagoon, it is necessary to examine both the physical and chemical stability of the tar, each of which are interdependent and must be controlled. Barriers to contaminant migration may be mechanically disrupted while physical barriers may be chemically attacked. Figure 9 depicts a conceptual model of a range of processes and potential migration pathways that have been observed or are inferred for a general acid tar lagoon.

Nichol (2000) reports results of investigations of an acid tar lagoon that indicate stratification of the tar into semi-solid layers separated by tar bands of softer consistency. Reynolds (2002) reports seismic survey data indicating softer surface tars underlain by more viscous tar. It is not clear whether this is simply due to differing batch properties as tar was placed in the lagoon, or due to long term separation or weathering processes. Semi-fluid tar, driven by the pressure head of the overlying tar and any capping material will find any cracks, and other pathways in the soil *e.g.* along tree roots or permeable soil zones. The acid will also tend to dissolve components of the mineral matrix helping to widen fissures and ease flow. Below the water table (as indicated in Section 5), tar will partially dissolve and may partially migrate in bulk.

6.2 Environmental Impact

While it is possible to infer and describe likely processes occurring in and around acid tar lagoons, there exists little scientific data to quantify many aspects of these processes or to establish their significance. Due to the inherent variability of tars it may also not be possible to generalise site and tar specific results in all cases. The available literature currently indicates that mechanical stability is a significant issue particularly with respect to unengineered capping layers, but also with the ability of the tar to flow through fissures in the ground and emerge some distance away. Leachability may be significant as has been discussed in Section 5.

Reynolds (2002) highlights the fire risk at acid tar lagoons. In 1980, the Lwyneinion lagoon had a layer of volatile hydrocarbon floating on the water overlying the surface tar. The volatile hydrocarbon ignited and burnt off, in the process evaporating the acid water and igniting the acid tar beneath. The resulting smoke plume necessitated the evacuation of a nearby town. The fire risk may be reduced by maintaining a water cover at all times.

Table 1 lists an extensive but not necessarily exhaustive set of potential linkages and environmental impacts of acid tar lagoons. Any restoration will seek to control these linkages to acceptable levels.

Table 1. Acid tar lagoons: potential linkages.

Source	Pathway	Receptor
BTEX, PAHs, VOCs	Volatilisation in upper soil surface	Site users
BTEX, PAHs, heavy metals, phenols & sulfate	Inhalation of dust and vapours	Site users, residents of adjacent properties
BTEX, PAHs, heavy metals, phenols & sulfate	Ingestion of surface soils	Site users, residents of adjacent properties
BTEX, PAHs, heavy metals, phenols & sulfate	Groundwater discharge	Nearby water course
BTEX, PAHs, heavy metals, phenols & sulfate	Surface run off	Nearby water course
BTEX, PAHs, heavy metals, phenols & sulfate	Migration along engineered structures (outfall)	Nearby water course
BTEX, PAHs, heavy metals, phenols & sulfate	Leaching/migration of contaminants through the soil and unsaturated zone	Major/Minor aquifer
Methane, sulfur dioxide and hydrogen sulfide	Migration through permeable soil	Site users, residents of adjacent properties
BTEX, PAHs, heavy metals, phenols & sulfate. Acid (burns)	Bulk migration of tar. Direct contact	Site users, residents of adjacent properties
Toxic combustion products	Smoke from combustion of tar in lagoon	Site users, residents of adjacent properties

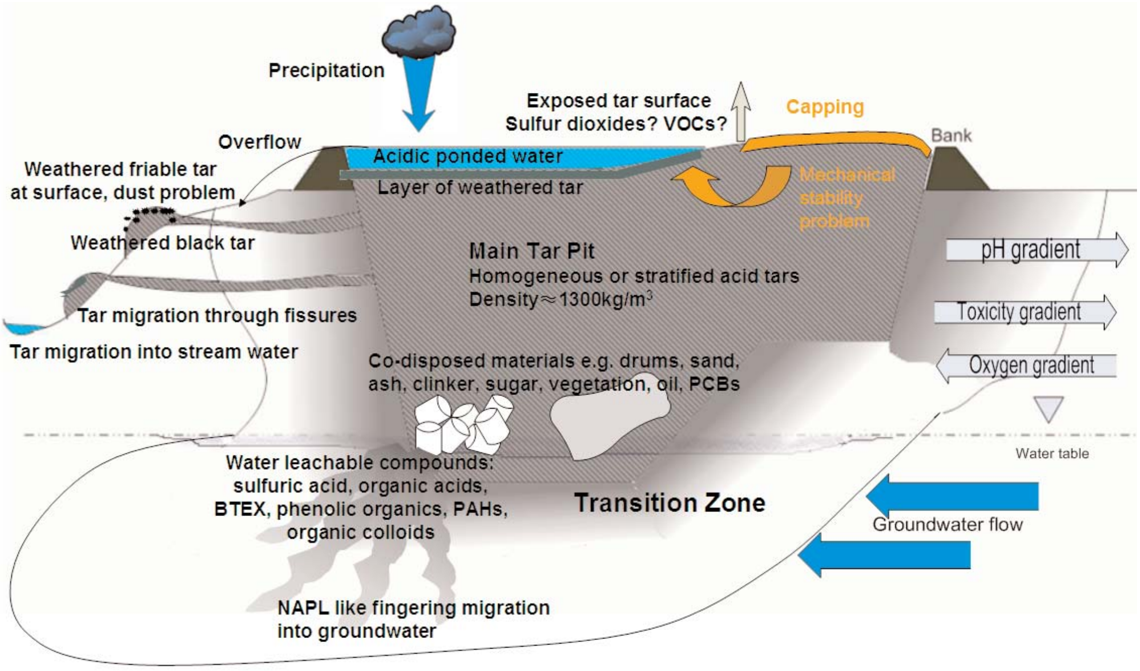

Figure 9: Conceptual model of generic acid tar lagoon processes.

7. REMEDIATION

7.1 Technical Issues

7.1.1 Monitored natural attenuation

In the absence of more proactive remediation solutions being identified, a number of UK acid tar lagoons are being regularly monitored to assess the impact on the hydrological environment. There is some evidence that acidophilic bacteria and algae may be able to degrade contaminants within surface waters, however, there is currently no evidence for such activity occurring within the body of acid tar deposits. Therefore, monitored natural attenuation may be appropriate as a short term measure to regularly assess the risk from sites where the principal environmental risk is related to surface water flow. This would include those lagoons that are uncovered, but otherwise well contained within excavations in impermeable strata. At these sites, surface waters accumulating from rainfall will require to be continually managed and some form of natural attenuation may be utilised for the organic contaminants.

However, the acid content of acid tars would be unaffected by biological processes and dilution and neutralisation by natural alkalis would have to be relied on. At the Hoole Bank acid tar lagoon in Cheshire, mass balance calculations, based on recorded historical rainfall patterns, measured site conditions and estimated total lagoon volumes, indicate that only 1.9% of the original sulfuric acid will have been removed by rainwater in the last 35 years. In acid tar lagoons that have been deposited in permeable strata and are subjected to groundwater flows, this rate of loss may be accelerated in proportion with the surface area exposed to groundwater flow. This may be further accelerated by the breakdown behaviour demonstrated in the flow cell tests. However, the down side of accelerated leaching and breakdown will be the size of the resulting pollution plume within the aquifer and the concentration of contaminants within it. In this latter situation the use of permeable reactive barriers coupled with continued monitoring may be appropriate.

The research indicates that natural attenuation is unlikely to be effective at removing the hazards associated with the body of acid tar lagoons over short timescales measured in tens or hundreds of years. In certain situations it may be acceptable to allow monitored natural attenuation to take place where the risks associated with pollution plumes leaching from an acid tar body are negligible.

7.1.2 Containment

As part of the research, the Building Research Establishment (Ridal, 2005) was commissioned to carry out a literature review of the durability of construction containment materials in acid tars and low pH ground waters. Table 2 lists the containment systems and materials that were considered. While Ridal concluded that there are a number of materials available, all have some advantages and some disadvantages with the maintenance of performance of the material in the environment over time being the most important issue. This maintenance of performance is affected by the degree the acid component of acid tars is neutralised by the addition of a base.

Ridal considered that cement-sodium exchanged bentonite in cutoff walls is likely to deteriorate by the sulfate and acidic components of acid tars but the material would be held together by the confining pressure of surrounding ground. He recommends that a high cement content should be used and Portland cement (Pc) should be partially substituted with both pulverised fuel ash (pfa) and ground granulated blast furnace slag (ggbs). Due to progressive attack, cement-bentonite cutoff walls would have limited design lives.

Table 2. Materials considered for possible use in containment systems (Source: Ridal, 2005).

Material systems	Details
Clay systems	• Cement-bentonite slurry cutoff walls • Natural clays • Modified clays • Permeable reactive barriers • Bentonite and plastic composites
Cement systems	• Concrete (Pc, pfa, ggbs) including concrete diaphragm wall barriers • Cement stabilisation and solidification including accelerated carbonation technology, injected grout encapsulation and dispersion by chemical reaction
Plastic membrane systems	• Polyethene (HDPE, MDPE, LDPE) • Polyvinyl chloride (PVC) • Polyamides • Polypropene • Polyesters

In respect of both natural clays and modified clays Ridal believes that they should be able to attenuate and physically contain all the components of acid tars, although the acid might attack the clays. This implies that a sufficient thickness of clay is needed to ensure that the design life of the containment system is met. Ridal also considered that permeable reactive barriers could have a role in attenuating the acid and cation components of acid tar but the anion and organic contaminants would be unaffected.

A lot is known about sulfate, chloride, acid and organic acid attack on concrete and the associated reactions leading to the respective formation of gypsum, ettringite, thaumasite, chloroaluminates and salt crystals. All of these, to a greater or lesser extent, lead to expansion, cracking and progressive deterioration of concrete. Ridal concluded that while partially replacing Pc with pfa or ggbs would help make concrete more durable for a limited design life in a containment system, ordinary Pc concrete should not be used.

Ridal also considered the use of plastic materials and concluded that all such materials would be subject to degradation through contact with the components of acid tar. This included polymer degradation, salvation, environmental stress cracking, microbial degradation and permeation. Ridal concluded that as all plastics are attacked by one or more acid tar components, plastics are not suitable for containing acid tars by themselves. However, there are a number of bentonite and plastic composites available as liners and these should be able to successfully contain acid tars for a limited period.

The literature review suggests that some materials may be suitable for short term containment purposes. However, it is recommended that this approach is only considered for lateral containment of acid tars on sites that are securely fenced off or are remote from residential areas and human health pollutant linkages are not significant. The evidence presented by those lagoons that have been previously capped with soil where tars have erupted through the capping layers suggests that this approach should be treated with considerable caution due to the high risk of failure within a relatively short time frame. Furthermore, the addition of capping materials may result in an increase in the volume of contaminated soils that will ultimately require remediation. If a mechanically stable and chemically resistant engineered cap is achieved, then the potential for build up of SO_2 and other (possibly flammable) gases beneath the cap should be considered.

If containment systems are considered, it is recommended that on-going monitoring be included as an integral part of the scheme to ensure failures are identified promptly so that remedial action can be initiated.

7.1.3 Excavation

For an acid tar lagoon to be removed, or be subjected to *ex situ* treatment, the material will need to be excavated. As discussed earlier, the emission flux of SO_2 increases five fold when acid tar is continuously disturbed. As a consequence the control of emissions to atmosphere is one of the principal difficulties associated with excavation works. In addition, the variable viscosity and presence of steel drums, unexploded bombs (Pensaert, 2005), and other wastes all add to the need for a robust and flexible excavation approach that can respond to changing site conditions.

Figure 10 shows the Mittlebach acid tar lagoon near Chemnitz in eastern Germany before excavation works began in February 2005 (a) and again in October 2006 (b). Despite the lagoon being located within 200 m of residential housing, BauFeld-Umwelt-Engineering GmbH successfully removed the acid tars using a gantry-crane, clamshell grab and long-arm tracked excavators. These placed the excavated acid tars into purpose-built, sealed transport containers. Maintaining a water layer over the acid tars as they were excavated minimised emissions while continuous monitoring of wind direction, wind speed and SO_2 concentrations allowed the work to be carried out safely. *In situ* oxidation of the contaminants within the surface water layer by the addition of hydrogen peroxide was also found to reduce emissions. The site staff were required to wear full protection including masks with activated carbon filters. These were also fitted to the drivers cabs on the excavators. The October 2006 photo shows the natural clay that was present beneath the lagoon. This clay had been used in the peripheral bund which is being progressively removed.

A smaller lagoon at Mittlebach, containing 2,000 tonnes of acid tar, was located within 50 m of residential properties. Here the material was successfully excavated within a tent which was maintained at a negative air pressure and equipped with air filters and scrubbers. The acid tar excavated from the Mittlebach lagoons was subsequently transported by road for off-site treatment. By October 2006 BauFeld had successfully excavated 150,000 tonnes of acid tar from four lagoons in the Chemnitz area for processing into a secondary fuel (see Section 7.1.5).

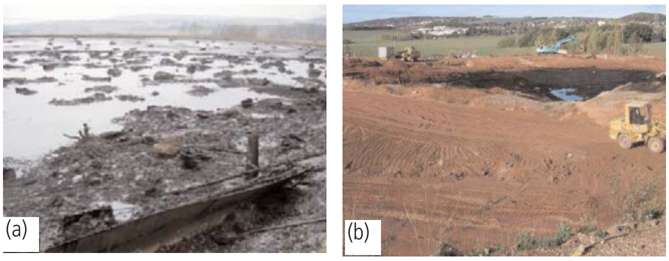

Figure 10: (a) Before (February 2005) and (b) towards end (October 2006) of excavation at Mittlebach acid tar lagoons, Chemnitz.

7.1.4 Solidification

DEC NV are currently involved in the excavation and solidification of 120,000 tonnes of acid tar at lagoons near Rieme, Belgium (Pensaert, 2005). These are also located close to residential properties and emissions of SO_2 to atmosphere require careful management. The solidification option was selected as the Best Available Technology Not Entailing Excessive Costs (BATNEEC) by the Flanders' Public Waste Authorities.

Following excavation the acid tar was taken directly into an on-site, purpose-built processing plant (see Fig.11). This was designed and built specifically for the treatment of the acid tars located in the lagoons (see Fig. 1). The output specification was to produce a solid and stable material suitable for a 10 m high 'landraise' located on site and complying with the criteria given in Table 3.

Figure 11: DEC solidification plant near Reime, Belgium.

Table 3: Output specification for solidified acid tar, Reime, Belgium (Source: Adapted from Pensaert, 2005).

Type	Criteria
Geotechnical	• Minimum Californian Bearing Ratio 11% • Compressibility modulus of 11 MPa • Maximum volume increase 30% • Maximum total consolidation settlement due to consolidation 5% • Maximum swell due to hydration 3%
Chemical	• Reduction in leachable hydrocarbon (expressed as Total Organic Carbon) by at least 90% • Minimum pH of 7 • Standard hazardous waste landfill leachability criteria for Flanders
Other	• Guaranteed stability of 10 years

An easy method to neutralise and stabilise acid tar is to mix it with quicklime. Unfortunately, this is a highly exothermic reaction which generates large quantities of toxic gaseous emissions. DEC experimented with alternative materials that also contained a proportion of free lime. These included blast furnace slags, fly ashes and municipal waste incinerator bottom ashes. Pensaert

(2005) found the most cost-effective result was obtained by using calcium oxide rich fly ashes as they were relatively cheap and also adsorbed SO_2. From experimentation a fly ash dose of 15% was found to be adequate for neutralising most of the acid tars.

The resultant mix was then solidified by addition of a combination of blast furnace slags and Portland cement. All of the dosing and additive mixing took place in the sealed treatment plant building which was maintained under negative air pressure and accessed via air locks. The final product was placed and compacted by vibratory roller. The final cost for the treatment of 120,000 tonnes of acid tar was estimated at €20m.

7.1.5 Use as substitute fuel

The cement industry is very energy intensive and both DEC and BauFeld considered the option of processing their respective acid tars into liquid substitute fuels for use in cement kilns. Gruss (2005) reported that in 1997 BauFeld trialled this approach and while the acid tars were successfully converted into a liquid fuel the process proved too expensive. It was also considered feasible by DEC for use in Belgium cement kilns but their client opted for the on-site treatment and solidification process (Pensaert, 2005).

BauFeld and their partner MUEG continued trials of processing the acid tars into liquid fuels for power station use. However, Gruss (2005) found that the frequency of breakdown of the pumps was a major problem with this approach and the conversion of the acid tar into a solid secondary fuel was more cost-effective. This approach was successfully adopted by BauFeld in 2000 and a purpose-built treatment plant was constructed at their Neukirchen acid tar lagoons. In this plant, wood chips were added to the freshly excavated acid tar to improve handling characteristics before the material was transported by sealed conveyor to a reaction vessel. Brown coal fly ash was then added in carefully measured amounts to neutralise the mixture. As gaseous emissions occurred throughout the process and particularly during the exothermic neutralisation process, the largest part of the plant was the forced ventilation scrubber unit and afterburner which were required to remove SO_2 and destroy volatile hydrocarbons.

The resulting material is a dry, friable substitute fuel that meets the acceptance criteria of the Swartz Pumpe power station. This power station is a modern, 2 x 900 MW brown coal fired plant commissioned in 2000. The acceptance criteria for the substitute fuel requires a calorific content of between 8.3 and 17.0 MJ/kg, a moisture content of less than 30% and a SO_2 content of less than 10%. A purpose-built reception hall and conveyor feeds the substitute fuel into the station at a rate of 85 t/hr; representing 5% of the total fuel feed.

The cost of completely remediating the second Neukirchen lagoon, including excavation, onsite treatment and final destruction as a substitute fuel of the 85,000 tonnes of acid tar, is estimated to have been €23m.

7.2 Social Science Issues

7.2.1 Legislative framework

While the examples of successful remediation projects cited above are located on mainland Europe, both Belgium and Germany operate under similar environmental legislation to England[2] that require tight process control and clean up standards. It could be argued that in Germany these go further than in England as remediation proposals are subject to a public inquiry process. As discussed below, this requires the full participation of all stakeholders.

In England the relevant legislation is Part 2A of the Environmental Protection Act 1990 and its related statutory guidance. This requires that local authorities identify contaminated land in their areas and ensure that it is managed in an appropriate manner. In order for a local authority to make a determination that a particular site meets the statutory definition of contaminated land, it must demonstrate that a significant pollutant linkage exists; that is, a source of contamination must be present together with a pathway and a receptor. The local authorities are required to create and maintain public registers of information on remediation notices that have been issued. Acid tar lagoons, are one of the classes of contaminated land that are defined by the legislation as "Special Sites", (see regulation 2(1)(b) Contaminated Land (England) Regulations 2000). As such, they still are identified and designated by the local authority but then the Environment Agency (EA) steps in to act as regulator. The EA's role is to carry out inspections of Special Sites and act as the enforcing authority to ensure that suitable remediation is undertaken to break the pollutant linkages. The UK approach to determining significant human health pollutant linkages is the Contaminated Land Exposure Assessment (CLEA) model, published jointly by the Department for Environment, Food and Rural Affairs (defra) and the EA (defra, 2002).

7.2.2 Stakeholder engagement

The examples of European acid tar remediation projects given above involved full stakeholder engagement. However, it is important to recognise the different interests and motivations of stakeholders and in particular the differences between internal and external stakeholders i.e. actors 'in the know' and able to directly influence the process, and less well informed people with limited influence but subjected to both short and long term effects (see Table 4).

Table 4. Primary interests and concerns of various stakeholders involved with contaminated land (Source: Talbot *et al.*, 2007).

Stakeholder- internal	Primary Interest and concerns
Site owner/s	Financial; cost/time benefit
Local Authority	Legal obligations, including environmental protection; income beneficial use of land; local amenities
Environment Agency	Protection of groundwater and surface water quality
National legislators/policy makers	Use of brownfield land to meet development targets
Health Protection Agency/ Primary Care Trust	Minimising risk to general public
Health and safety officers	Protection of remediation contractors
Remediation consultants	Clients interests
Remediation contractors	Narrow contractual obligations
Stakeholders- external	
Local politicians	Local electorate
Media	Story, sensationalizing issues
Local community	Property values; safety; local amenity value of site.
Wider community	Area amenity value

During the SUBR:IM research, interviews were carried out with a number of different stakeholders involved with a particular acid tar lagoon. The lagoon had split ownership and was partially covered, it was also located in close proximity to residential properties, a stream and groundwater resources. The covered part was used as an area of informal public open space. It had the potential to be causing harm to each of these classes of receptors and had been subject to a number of investigations, risk assessments and temporary remedial actions over a number of years. The Local Authority, as primary regulator, was in the process of considering designating the site as a Special Site. However, it was interesting to receive the following diverse comments from the key stakeholders following the production of the latest human health risk assessment of part of the site by consultants to the EA:

- The Local Authority, believed the assessment to be flawed but felt compelled to react, despite its apparent flaws.
- The EA case officer indicated the Agency's preferred option (in response to the risk assessment) would be urgent action such as fencing to secure the site followed by remediation. Blight was recognised as inevitable, but with designation it would look as if something was being done.

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[2] It should be noted that the policy approaches adopted in Scotland, Wales and Northern Ireland are similar to the one that operates in England. Generally, comments referring specifically to England in the following paragraphs can also be applied to the UK as a whole.

- A representative from the private company that owned the fenced off part of the site expressed little concern about potential liabilities or political fall-out because the risk assessment did not cover their side of the site.
- The Lead Member for the Environment in the Local Authority saw a need to take action based on the risk assessment, however, noted that financial resources were a prime consideration and contaminated land had a low priority in budgetary terms.
- Two local Ward Councillors considered it a desirable place to live and that resident's only concern appeared to be the possibility of the site being developed and the consequent loss of their recreational area. They also indicated that local residents did not consider themselves to be at risk, despite an acute awareness of the history of the site.
- The Neighbourhood Manager for the Local Authority, responsible for co-ordination between various actors and agencies operating in the area and liaison with the public, was unaware of any particular concerns about the site.

Some form of open engagement with two way communication would help bridge the gap in perspective illustrated above. It is often identified that best practice in communicating contaminated land risks is to be open and transparent with the general public at an early stage. Open processes of communication can help to generate trust between decision-makers and affected communities.

It is suggested that the European examples of acid tar remediation projects have been successful as the diverse, and sometimes narrow, interests of the various stakeholders have been aligned by active stakeholder engagement to a single common goal of removing the acid tar hazard in a controlled and closely regulated process.

The sustainability of the two European acid tar remediation projects discussed above, and the use of these approaches within the English regulatory system, were considered by a group of EA officers at a SUBR:IM seminar and workshop held at the EA's Leeds office on 20 June 2007. A number of views expressed that the sustainability of a project could only be assessed following a full life cycle and cost/benefit analysis. While a number of delegates considered that conversion to a substitute fuel and subsequent destruction appeared to be a sustainable solution, it was suggested that the conversion of stabilised material into a construction material may be more sustainable. That said, there was concern over the long-term performance of the stabilised material. As both offsite and onsite treatment options would involve transportation of bulk materials an assessment of road-mile/tonnes was a critical factor in any sustainability analysis. It was also clearly stated that the most appropriate remediation solution is controlled by local factors and what may be sustainable at one location will not necessarily be sustainable at another. In respect of more general comments relating to the English regulatory regime it was also noted by the delegates that the English regime needs to change from being 'process' focused to 'outcome' focused. Furthermore, the delegates also noted that under the existing regulatory regime the local authority decisions on contaminated land remediation are subject to political pressures and budgetary constraints.

This feedback is considered valuable as it identifies the importance of life cycle and cost/benefit analysis in choosing between options for remediation projects in England. It was also useful in identifying potential weaknesses in England's current regulation regime. While the English regulatory regime may make it difficult to align stakeholders interests, the system is not sufficiently flawed to preclude the adoption of sustainable acid tar remediation options within England.

7.2.3 Funding

England's contaminated land legislation is based on the 'polluter pays' principle. However, in respect of acid tar lagoons that have been around for many decades, the original polluter may not be found or may no longer have sufficient funds available to successfully remediate their sites. In these cases or where the site is in local authority ownership or is the responsible person for the contamination, local authority and/or the EA have the opportunity to access funding to investigate and remediate designated sites through the Contaminated Land Capital Projects Fund administered through defra.

8. SUMMARY

Some information on acid tars and acid tar lagoons has been previously published. The authors' recent research has built on this and has attempted to fill some of the knowledge gaps. In so doing, physical, chemical and biological properties are considered together with weathering and leaching behaviour and environmental interaction. Finally, practical, technical and social science aspects of remediation are discussed. Although acid tars present complex and challenging problems, the case studies covered by the research indicate that a range of remediation solutions are available. However, when selecting between appropriate remediation options the sustainability, as demonstrated through life cycle and cost/benefit analysis and stakeholder engagement, is a key factor to be considered. Furthermore, due to the relative small size of acid tar lagoons in the UK and the scale and cost of infrastructure required for permanent remediation solutions, it is anticipated that sustainable remediation will only be possible if a coordinated and strategic approach, that tackles several acid tar lagoons together, is undertaken. This may be difficult to achieve under the existing regulatory regime.

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