Acid Tar Lagoons: Assessment and Environmental Interaction

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Summary

Acid tars are waste residues of obsolete benzole refining, oil re-refining and white oil production processes. They are black, acidic, viscous semi-liquids comprising an extremely complex mixture of water, sulfuric acid and a large range of organic compounds. Acid tars were often dumped into excavations and existing holes in the ground together with various co-disposed materials without any treatment or engineered lining system leaving a legacy of acid tar lagoons. Acid tars may pose potential risks to human health and the environment because of their acidity, volatiles and other hazardous components. The major contamination pathways of acid tar lagoons are considered to be direct contact, gas emission, bulk tar migration offsite, and surface and ground water contamination.

The leaching, weathering and migration behaviours of acid tars were investigated by carrying out a series of batch, cascade and flow cell tests. The results demonstrated that acid tars are capable of leaching significant levels of contaminants if disturbed, while the leaching level is significantly lower under simulated groundwater flow in a model soil. The time scale to leaching stabilization was of the order of months in the model soil and is expected to significantly exceed that in the natural environment.

To support this work a nubmber of analytical methods for determining physical and chemical properties of acid tars had to be adapted from standard techniques. These modified techniques are described in detail together with recommendations for data integration and correlation of all analyses to form a better understanding of acid tars and their potential environmental impact. The overall findings of the research were integrated to generate a conceptual model of acid tar lagoon processes to assist in assessment. Monitored Natural Attenuation was evaluated and is considered to be a potentially viable approach to the environmental management of some acid tar lagoons.

Chapter 1 Introduction

1.1 Acid Tar Lagoons

Acid tar lagoons are a significant source of contamination that is a hazard to human health, controlled waters and the natural environment. Acid tars are normally defined as tars of high sulfuric[1] acid content that have arisen as by-products of benzole refining, refining petroleum fractions (particularly white oil) and oil re-refining. A common disposal method was to dump them in existing holes in the ground to form lagoons. In-situ, acid tar comprises a mass of hydrocarbons that is generally viscous with very low pH. Surrounding soils are likely to be contaminated to varying degrees with tars and hydrocarbons. Many of these acid tar lagoons are situated in close proximity to residential areas. Despite being a worldwide problem, the coverage of acid tar lagoons in the scientific literature has been minimal and only in the last few years have remediation options, acceptable under modern regulations, been developed. However, a large gap remains in our understanding regarding the processes occurring within acid tar lagoons and the interaction between the lagoon and the surrounding environment. These are essential to inform a decision making framework for setting remediation priorities for current acid tar lagoons.

1.2 Research Context

This PhD research formed part of the SUBR:IM (Sustainable Urban Brownfield Regeneration: Integrated Management) work package H: "Restoration of Acid Tar Lagoons". This multidisciplinary work package

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[1] The element has traditionally been spelled *sulphur* in the United Kingdom, Ireland, Hong Kong, the Commonwealth Caribbean and India, but *sulfur* in the United States. International Union of Pure and Applied Chemistry (IUPAC) adopted the spelling "sulfur" in 1990, as did the Royal Society of Chemistry Nomenclature Committee in 1992. The spelling of the term in non-official texts is gradually becoming uniform as *sulfur*. Sulfur is used in this thesis.

combined both science and social science research. Scientifically, the goal of the research is to find a way to understanding problems at acid tar lagoons in general and specifically at two particular study sites that have both general and distinctive features. An additional aim of this work package was to test ways of communicating and working with local communities at difficult sites in the development of remediation strategies acceptable to all stakeholders. This socio-economic research was conducted by colleagues of Greater Manchester Geological Unit (GMGU). This PhD research focuses on the science side of acid tar lagoon problems, drawing upon limited previous knowledge of acid tars, with the broad aim of improving understanding of the material, its environmental impacts and sustainable ways of dealing with it.

1.3 Research Objectives

Previous approaches to the treatment of acid tar lagoons have focused mainly on source removal. However the environmental impacts of acid tar lagoons have not been fully addressed. Data derived from a number of site investigation reports from acid tar lagoon sites indicates that the interaction between the bulk tars and the surrounding area is limited. However, several processes have been observed at the edges of acid tar lagoons which make acid tar lagoon a unique type of brownfield land that can modify the site physically, chemically and biologically. Therefore, the thesis that will be tested in this work is that for certain acid tar lagoons, Monitored Natural Attenuation (MNA) is potentially a viable approach for the environmental management of acid tar lagoons.

The specific research objectives of the PhD project are:

1. Fully characterize acid tars, including physical properties and chemical composition, to identify all potential contaminants in acid tars and enhance understanding of the behavior of acid tars.
2. Investigate the behavior of acid tars in a lagoon environment, including

their migration, leaching of water soluble components and weathering, to identify contaminant pathways from acid tar lagoons and therefore guide the development of remediation options that focus on controlling these pathways.

3. Develop a conceptual model of acid tar lagoons based on the data above.
4. Evaluate MNA as a potential sustainable approach to dealing with acid tar lagoons.

1.4 Research challenges

From the outset, this PhD project had a number of challenges. The research started from a very wide perspective. Acid tars are fairly new research topic and at the start of the project there were only 3 core references in the literature, all of which focused on reporting production, historical disposal and previous remediation methods attempted at various acid tar lagoons. The project was thus unusual in that most of the research had to start from baseline, e.g. handling of the material, elucidating its broad behavioral patterns before defining detailed test programs etc. During the sampling on the two study sites, only limited samples could be collected on one site due to regulation, health & safety issues and the concerns of the site owners. Furthermore, only surface and shallow depth subsurface samples were available in the second study site for testing and laboratory work due to the lack of heavy machinery and health & safety concerns of sampling from the main lagoon.

In the second year of this research, the analytical lab of the department was moved to another location, which delayed all analytical experiments for a 6 month period. This gave the project an unusual pause with regard to the analytical work but did provide an opportunity to review all completed tests. Some additional trial tests on other issues of acid tars such as column leaching and mechanical properties were carried out during this period which provided additional information for the project.

Chapter 2 History, Production, Nature and Disposal of Acid Tars

2.1 History of Acid Tar Lagoons

Up to the First World War, UK acid tar production arose primarily as a waste residue from a by-product recovery process used in the coal carbonization industry. Acid tar was also produced by the oil refining industry and most recently, the petrochemical industry. The production did not cease until the 1980s, when the first two industries shrunk to a minimal scale and new technologies had been invented for petrochemical processes.

Acid tar lagoons exist in a number of countries in the world but information on scale or production is limited. Gruss (2005) reported oil refinery acid tar lagoons in Neukirchen and Mittelbach in Germany that operated up to 1989. Pensaert (2005) reported on 3 acid tar lagoons in Rieme Belgium, that operated during the early and middle 20th century. Grajczak, 1995 also reported acid tar sludge at the Sand Springs Petrochemical Complex of Oklahoma State, USA arising from a petroleum refinery operated since the early 1900s.

2.1.1 Production Processes

Acid tars are produced by three main processes: benzole refining, oil re-refining and white oil production, all of which involved the use of concentrated sulfuric acid to purify an organic material. (Nancarrow *et al*, 2001)

Crude benzole is a by-product of coal carbonization, a process that produces coal gas (mixture of H_2, CO, CH_4 and volatile hydrocarbons with impurities such as CO_2 and nitrogen), coke and coal tar. Crude benzole is the lighter fraction of coal tar that can be collected by the condensation of organic vapours and is capable of recovering benzene, toluene and xylene fractions for industrial use. The benzole refining industry therefore boomed in the early twentieth century. Concentrated sulfuric acid was used by industry to remove two major impurities: sulfur containing compounds and unsaturated hydrocarbons. Crude benzole was washed in either batch or continuous washers and the acid tars were run off from bottom of the washer as a residue while benzole was collected for further processing. (Claxton, 1961 and Miline *et al*, 1986)

Oil re-refining refers to the regeneration of spent lubricants for either direct use or for re-use in other applications, such as a base stock for blending with fresh oils (Slater, 2003). Concentrated sulfuric acid is used to remove dissolved metal impurities, unsaturated organic compounds and sulfur containing compounds. Addition of clay (Fullers Earth) was also used as a filter to aid the absorbing of residual acid, sludge and any remaining solid material. Acid tars produced from oil re-refining may contain such spent clay. (Miline *et al*, 1986 and Nancarrow *et al*, 2001)

In the petroleum industry, the use of concentrated sulfuric acid as a washing agent was formerly widespread, but has been drastically reduced due to the introduction of economically and environmentally better methods, such as catalyzed processes. However acid treatment is commonly applied to the production of white oils, which are highly purified compounds used for medical, cosmetic and specialized lubrication purposes. In common with the other two processes, sulfuric acid is used to remove unsaturated and sulfur containing compounds. Furthermore, to enable sulfonation and removal of aromatics, sulfur trioxide and/or fuming sulfuric acid are also applied, which make acid tars produced by white oil production some of the most hazardous and dangerous to human health and the environment. (Miline *et al*, 1986 and Nancarrow *et al*, 2001)

It can be concluded that, although all called acid tars, material produced from above production processes can be highly different in composition and properties. In addition, acid tars produced from same processes can be highly differentiated due to the starting material, production conditions and other factors. No two batches of acid tars produced are the same. The heterogeneous nature of acid tars is, therefore, one of the major features of acid tars that has to be borne in mind in the research.

2.1.2 Scale of the Problem

Acid tar production has been reported in the UK, mainland Europe, Russia, Australia and North America. Detailed production data worldwide is very limited. Acid tar lagoons reported by Gruss (2005), Pensaert (2005) and Grajczak (1995) contain 100,000 tonnes, more than 200,000 tonnes and 135000 cubic yards of acid tars respectively.

In the UK, according to the Environmental Agency's record, there are approximately 150 acid tar lagoon sites, varying in size, and possibly more unrecorded sites. There is limited information available on production figures and site records in the public domain. The available information is mainly derived from Environmental Agency R&D reports on acid tar lagoons by Nancarrow *et al* (2001), which are summarized below.

The benzole refining industry started during the First World War when the need for toluene for explosives arose, the industry boomed during and after Second World War and reached its peak in the late 1950s/early 1960s. Benzole refining then declined due to the growth of the petrochemical industry and the decline of the steel industry (the main user for coke). The production of acid tars can only be estimated due to the lack of detailed records. It is indicated that at the peak of production, approximately 90,000 tonnes of acid tar was produced each year and the production soon declined to 15,000 tonnes per year in 1982 and 4000 tonnes per year by 1985. The benzole refining plants were usually small to medium scale and acid tar lagoons raised from these plants were consequently small/medium in size.

The oil rerefining industry is a small industry. It is started up during the

Second World War and declined in 1980s. It is estimated that 25,000 tonnes of acid tar were produced in 1971 and 9000 tonnes in 1985. The oil rerefining production sites were usually small in scale.

Acid tars produced by the white oil production industry developed and grew rapidly during and after the Second World War. The production reached 100,000 tonnes per year in its peak period and shrunk significantly because of the introduction of catalytic methods for most processes. The scale of petrochemical processing plants was usually big and consequently acid tar lagoons near those sites are mostly large in size.

2.1.3 Acid Tar Lagoons

Historically, acid tars produced by any of the three processes were usually dumped into old quarries, clay pits or other existing holes in the ground near the production plants due to the lack of regulation. The scale of the dumping is unclear prior to 1972 before the Deposit of Poisonous Wastes Act (DPWA) was introduced. After this date, the dumping was more engineered but still not well controlled. The co-disposal of other hazardous waste, such as drums containing chemical wastes, sand, ash, clinker, sugar waste etc, made the environmental problem of acid tar lagoons more challenging. The ground conditions at each lagoon will be site specific, which in turn given rise to site specific lagoon problems.

There are only limited number of acid tar lagoons in the public domain. Hoole Bank, an uncapped acid tar lagoon in Cheshire, England (Nichol, 2000) is a relatively compex site and was used as major study site for this PhD study. Another capped acid tar lagoon in North West of England was also selected as study site because both of its technical and social science interests. By the request of the site owners, this site has to remain anonymous. Other UK acid tar lagoons in the public domain are Cinderhills near Belper in Derbyshire (Carney, 2007), and Llwyneinion near Wrexham, Wales (Reynolds, 2002).

2.2 Nature of Acid Tars

Although in general acid tars may be heterogeneous between and within sites, there are common, fundamental acid tar characteristics. The characteristics may be categorized into physical properties, composition and chemical properties as summarized below.

2.2.1 Physical Properties

Acid tars can be described as black or brown colored, viscous material with very high acidity and a strong, acrid odour (Milne *et al*, 1986). Physical properties are summarized in Table 2-1.

Origin	Viscosity	pH	Colour	Odour
Benzole refining	Thin to fairly viscous	pH 2 or lower	Generally black	Strongly aromatic
White oil production	Very viscous	The most acidic tars, pH below 1	Generally black	Oily
Oil re-refining	Variable	pH 2 or lower	Browner than others	Oily

Table 2-1 Physical properties of acid tars (Nancarrow *et al*, 2001)

The viscosity of acid tars is highly temperature sensitive. Acid tars tend to be more fluid and mobile at higher temperatures and become fairly solid when the temperature drops. At exposed surfaces, weathering may result in an irreversible increase of viscosity within the lagoon surface layers.

The density of acid tar has been reported at between 1200 and 1400kg/m^3 (Nichol, 2000), which is higher than typical coal tars at 1060 kg/m^3 (Oudijk and Coler, 1995). It is assumed that the higher acid tar density is due in part to the high sulfuric acid content (density 1960 kg/m^3).

2.2.2 Composition

The composition of acid tars varies due to the different production processes and from site to site. When dumped on site, the addition of co-disposed materials makes the composition even more complicated. Excluding the co-disposed materials, acid tar generally consists of water, sulfuric acid and a large range of organic compounds that are soluble in sulfuric acid. The water content of acid tars has been reported as up to 50% by weight and sulfuric acid content may be up to 60% but can be as high as 90% by weight in some extreme cases of acid tars produced by white oil production (Nancarrow *et al*, 2001). Nesbit *et al* (1995) also suggested that three phases exist in acid tars, which are (i) a low mobility free tar phase that comprises mainly of high molecular weight asphaltenes and other polar hydrocarbons, (ii) a free flowing oil phase composed predominantly of mid-distillated saturated hydrocarbons and finally (iii) made ground and natural strata contaminated by a high concentration of sulfate and acids. Nancarrow *et al* (2001) suggested similar phases (i) and (ii) but described phase (iii) as a sulfate rich acidic aqueous phase. It is likely that, with respect to this third phase, Nesbit *et al* were addressing contaminated soil at the base of the lagoon while Nancarrow *et al* were addressing contaminated top water at open, uncapped lagoons.

The organic species within acid tars can be categorized into two groups, hydrocarbon species and organic acids. Hydrocarbon species within acid tars include oils (paraffins, naphthenes and aromatic hydrocarbons: heavier polycyclic aromatics and lighter monocyclic and bicyclic aromatics), resins and asphaltenes. The organic acids mainly comprise various sulfonic acids that are generated during the production processes and a fraction of carboxylic acids. (Frolov *et al*, 1981 and Topilnitskij *et a*l, 1996). The major potential hazardous organic components of acid tars are expected to be Polycyclic Aromatic Hydrocarbons (PAHs), phenols, Benzene, Toluene, Ethylbenzene and Xylene (BTEX) and sulphonic acids.

It should be noticed that most of the literature that has data on acid tar composition was published in the 1980s or earlier before acid tar production ceased. The composition of dumped acid tars could thus change due to the leaching of mobile components such as sulfuric acid and volatiles. Some of the later literature show a decline in acidity (Topilnitskij et al, 1996)

2.2.3 Chemistry of Acid Tars

The complexity of acid tar composition makes the chemistry of acid tars extremely complicated and very hard to fully understand. There is very limited literature in this area. The major features of acid tars that separate it from coal tar or other organic mixtures are its high acidity and the sulfonic organic compounds. During the production processes, unsaturated hydrocarbons can be attacked by sulfuric acid and sulphonated into sulphonic organic compounds (Senning, 1972). Sulphonic organic compounds are acidic, which contributes to the acidity of acid tars and are also capable of releasing sulfur dioxides under heating or other conditions, which is a major challenge when handling acid tars. Bukharkina *et al* (1993) and Zharkikh *et al* (1994) studied the thermal decomposition of acid tars at temperature ranges of 120 -160°C. It is also reported that acid tars can release sulfur dioxides at lower temperatures by heating or by physical disturbance (Kerr and Probert, 1990; Gruss, 2005).

2.3 Environmental Impacts of Acid Tar lagoons

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 generalize site and tar specific results to other cases. The available literature currently indicates that mechanical stability is a significant issue particularly with respect to capping layers, but also with the ability of the tar to flow through fissures in the ground and emerge some distance away. 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 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 generalized. Banks *et al* (1998) 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).

The emission of sulfur dioxide is another major environmental problem of acid tars. Acid tar is capable of releasing sulfur dioxide when exposed to the air though acid tar lagoons covered by water may prevent or attenuate such an emission. Pensaert (2005) highlighted the sulfur dioxide emission problem during the stabilization treatment of acid tars in acid tar lagoons near Rieme Belgium. The measurement of emission flux from different types of acid tars (all arising from refining of oils) indicated that: (i) sulfur dioxide was one of the main compounds released; there was no hydrogen sulfide found in the emission while only a minor amount of VOCs are detected; (ii) the emission flux was not significantly influenced by wind speed, which indicated that the sulfur dioxide emission was determined by diffusion; (iii) the average sulfur dioxide fluxes from different types of tar are 1g/(m^2.h) for liquid tars, 12g/(m^2.h) for viscous tars and 500g/(m^2.h) for solid tars. (iv) the emission flux increased with about 5 times when acid tars were continuously disturbed and the flux can be reduced by covering the tars with a thin layer of lime slurry. Bukharkina *et al* (1993) and Gruss (2005) have also reported sulfur dioxide emission of acid tars.

Nancarrow *et al* (2001) indicated that fire hazards may be present at some sites, especially those from benzole refining where BTEX compounds will be present but also at other sites. Burning of acid tars in lagoons was sometimes practiced in the past to improve stability of acid tar lagoons. Reynolds (2002) also 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 of acid tar lagoons are highly site specific and likely to be limited to acid tars arising from benzole refining. The fire risk from acid tars produced by oil rerefining or white oil production is most likely caused by co-disposed materials rather than acid tar itself. These acid tars contain mainly heavy organic compounds containing 15-35 carbon atoms (C15-C35) or heavier aliphatic and aromatic hydrocarbons (Carney, 2007). The auto-ignition temperature of such a mixture is usually very high (coal tar oil: 580°C, heavy hydrocarbons 750°C by The Engineering ToolBox 2005). So it is unlikely that those acid tars posses a high fire risk itself. During a site visit to an oil re-refining acid tar lagoon site, a burnt out car had been observed half sunk in the middle of uncapped lagoon surface, which is further evidence that acid tar, especially for acid tar arising from oil re-refining which containing less volatiles, is not normally capable of being ignited.

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

Table 2-2 Pollutant linkages of acid tar lagoons (Nancarrow et al, 2001)

Nancarrow *et al* (2001) summarized the potential pollutants linkages of acid tar lagoons as reproduced in Table 2-2. Any restoration will seek to control these linkages to acceptable levels.

2.4 Remediation and Utilization

2.4.1 Pathway Control

Pathway control techniques break the contamination linkages between the source and receptors. The most common technique used for acid tar lagoons was capping, which used clay, soil or alkaline material such as fly ash to cap the open acid tar lagoon surface. Capping is a simple, easy and economical choice of treatment of acid tar lagoons. It breaks most of the contaminant pathways and pollution linkages. However, the capping soil is usually heavier than the acid tar itself, which thus pressurizes the main tar body, and encourages bulk migration of acid tars off site often resulting in more problems. There was an effort to cap Hoole Bank, the main study site, using wood sticks and soil in early 1990s which resulted in the sinking of all capping material and the raising of the lagoon above ground level. A bund had to be built to contain the raised acid tars. Acid tar migration has also been observed in the other study site at various locations, and at the Cinderhills site (Chambers, 2001 & 2005) .

2.4.2 Source Control

Source control techniques achieve remediation of acid tar lagoons by rendering the acid tars inert or completely removing the acid tars and the associated contaminated ground. A highly significant challenge to carrying out any removal is controlling emissions during operation. As discussed in Section 2.2.3, acid tars may release significant quantities of sulfur dioxide when disturbed, which is harmful to human health and is one of the major source of acid rain (Carey, 2001). Therefore, the control of sulfur dioxide during in-situ operation has to be considered for any source control techniques. Gruss (2005) utilized sophisticated monitoring and emission control systems such as high power air blowers for large sites or gas control tents for small sites.

2.4.2.1 Pre-Treatment

Acid tars that were produced 20 years ago or before were mostly dumped with limited or no pretreatment. Only some acid tars produced by benzole refining were pretreated by passing acid tar through water or water steam to reduce their acidity and recover some of the sulfuric acid (Claxton, 1961). The history of the capped study site also described mixing acid tars and limestone to neutralize acidity before landfill. However this process proved unsuccessful because the acid tars were too vicious to be mixed efficiently.

2.4.2.2 Stabilization/Solidification

The stabilization/solidification approach to acid tar treatment is reported by Lagrega (1990), Grajczak (1995) in the USA and more recently Slater (2003) in UK and Pensaert (2005) in Belgium. In general the technique blends acid tars with fly-ash, lime, cement, bentonite or specially clays resulting in a physically stronger, chemically stabilized material that has a reduced environmental impact. The challenges faced by the technique are SO_2 emission control during disturbance of the acid tars, high use of energy by the mixing process and volume increase of the final product. Furthermore, the end product itself is still potentially a hazardous waste. If the stabilization degrades over time it maybe even harder to deal with in the future.

2.4.2.3 Incineration

Incineration of acid tars, utilizing it as an energy source has been investigated by several authors. Miline *et al* (1986) suggested incineration as the most efficient techniques of acid tar treatment. Kerr and Probert (1990) used a fluidized-bed combustor to burn acid tar waste with addition of limestone as bed material for sulfur capture, which resulted in 417ppm of sulfur dioxide emission in the exhaust gas, which exceeded the UK Air Quality Objectives (should not exceed 350ppm of 1 hour mean for more than 24 times a year). Baruah and Phukan (1995) reported the use of acid tar as a binder for coal briquette or a solid fuel for industrial furnace turning acid tars into neutralized and dried mass in Digboi, India. Tumanovskii *et al* (2004) produced an energy carrier (fuel) out of the bottom layer of acid tar and burnt it in a circulating fluidized bed to produce electricity in Russia. Most recently, Gruss (2005) in Germany treated acid tar lagoons by using a mobile process plant to convert the acid tar to a stable form suitable for use in a brown coal power station. The technique, however, is only economical and feasible for large scale acid tar lagoons. Smaller acid tar lagoons or acid tar lagoons with limited space or access or acid tar lagoons close to residential area, are more challenging.

2.4.2.4 Utilization

Frolov (1980) & (1981) discussed the using of acid tars as paving asphalt in Russia and Topilnitskij (1996) discussed the production of bitumen and water-repelling cement from acid tar wastes in Ukraine. Both authors focused on the mechanical properties of the product without addressing the potential problems of the hazardous components. Thus significant further work is required to pursue these approaches in a modern regulatory framework. Baruah and Phukan (1995) reported using neutralized and dried acid tar as binder for graphite electrodes, which could be an innovative approach for utilizing of acid tar.

2.5 Summary

A literature study of the history, production, properties and previous remediation activities of acid tar lagoons has provided background information to acid tar lagoon problems and highlighted limited previous research into several interests of acid tar lagoons. Significantly, there was insufficient scientific data, especially on the physical and chemical properties of acid tars, in the literature to enable the detailed methodology for this research to be fully defined. Furthermore, since some of the information in the literature was published more than twenty years ago, the characteristics of acid tars could change during this period. Site visits, therefore, were carried out to gather further information of concerning acid tars and acid tar lagoons.

Chapter 3 Acid Tar Lagoons: Site Characteristics

A number of site visits, sampling and preliminary test activities were made to four acid tar lagoons in North England during the initial stages (2004-2005) of the PhD in order to better understand the problems of acid tar lagoons, heterogeneous characteristics of various lagoons and to gather information and samples for laboratory tests.

One of the main features of acid tars that is not covered by the previous literature is the formation of various forms of acid tars on site by migration and weathering processes. The weathered acid tars have distinct physical and chemical properties that render the study of acid tar lagoons more complex while potentially providing an opportunity to develop innovative management strategies. Identified acid tar forms are viscous acid tar, weathered black tar, weathered particulate tar, weathered green tar and weathered crystalline tar. Detailed discussion on weathered forms of acid tars is covered in Chapter 6.

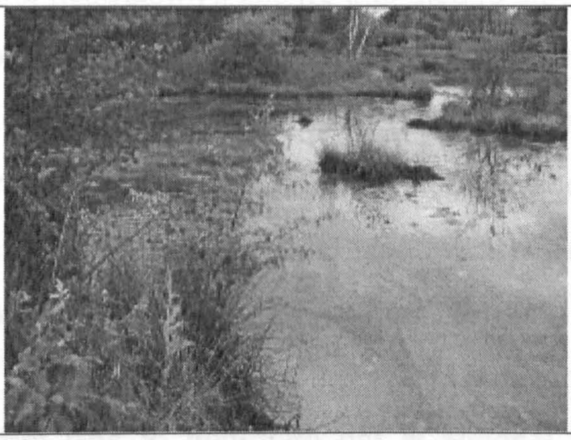
Another main feature of acid tar lagoons is the migration of acid tars. Evidence of migration was found on every visited site through various routes, including overflow, migration through fissures in the ground, migration through tree root zones and large scale bulk migration from the main lagoon. The driving force of the migration is usually pressure of capping soil or self weight of acid tars.

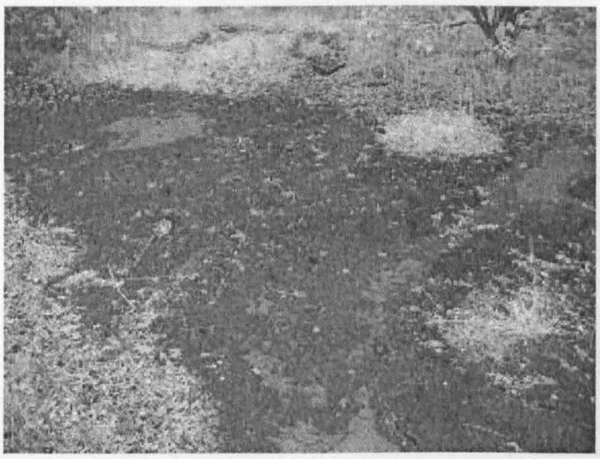
Excavation of several weathered tars at Hoole Bank and on-site penetrometer tests indicated the structure of the main lagoon and weathered locations, at depths reachable by the penetrometer. The main lagoon had ~30cm of surface water, 20-30cm of hard crust, identified as weathered green tar, and deeper viscous tars. A weathered location near the bund of the main lagoon had a layer of clay-like weathered black tar and deeper viscous tar. At a weathered location away from main lagoon, weathered friable tar was found on the surface with hard, non-flexible weathered black tar underneath and occasional dark green colored, extremely hard crystalline tar. There was no distinct interface between the layers.

Microbiological activities were observed in the ponded acidic surface water (pH 2.84-2.92) at Hoole Bank. Significant quantities of brown green colored "pond weed", later identified as algae, was found.

Key features of acid tar lagoons identified by the site visits are summarized in Figure 3-1.

Figure 3-1 Features of Acid Tar Lagoons

Photo Evidence	Acid Tar Lagoon Features
	**1. Lagoon Top Water:** Because of acid tar's low permeability, an uncapped acid tar lagoon usually accumulates rain water that forms a surface layer. The lagoon top water is contaminated by sulfuric acid, soluble organic compounds and soluble contaminants from co-disposed materials, such as iron, aluminum or other heavy metals etc.
	**2. Oily phase organic contaminants:** Free oily phase contaminants (NAPLs) usually floating on the surface of lagoon top water or bound to mud and humus matter at bottom of the lagoon top water, which can be released by disturbance.

	**3. Black Coating of organics:** Organic contaminants in acid tars that have entered the surface water are found adsorbed by soil at the lagoon edges forming a thin black coating around the main lagoon.
	**4. Top Water Overflow:** Lagoon top water sometimes flows over or seeps through the bund of main lagoon and causes more contamination.
	**5. Weathered Tar Surface:** Capped acid tar lagoons usually feature exposed weathered acid tar because of acid tar migration. Mobile viscous acid tar driven by the pressure of heavier capping soil finds its way up to the surface through weak points of capping layer. Viscous acid tar dries and loses its mobility during migration on the surface. Acid tar is more mobile during summer seasons due to high temperature and high precipitation level.
 2003/02/17	**6. Weathering - Weathered Black Tar:** Weathered black tar is an intermediate weathered form of acid tar. It is usually found in the pathway of surface acid tar migration. Weathered black tar is rubbery, flexible material that can have clay-like properties and relatively mobile.

	**7. Weathering – Weathered Friable Tar:** Weathered Friable tar appears as a final form in the weathering process. It is weathered from weathered black tar through loss of the water content and organic solvents that bind the mixture together. It is usually found at the end of migration pathways and is light, weak material that can be transferred offsite by wind blow.
	**8. Weathering – Weathered Crystalline Tar:** Weathered crystalline tar is another final form of weathered tar. This example was found at a large, deep section of acid tar migration. It is very strong but non-flexible material that formed under the cover of weathered friable tar.
	**9. Migration – Pond of Viscous Tar:** Sometimes viscous acid tar migrates in bulk from the main lagoon and upwells to form a pond of viscous tar which is covered by thin layer of weathered particulate tar. It is soft and deep that can be dangerous to site visitors.
	**10. Migration – Tar migration through minor cracks:** In other cases, viscous acid tar can also migrate through minor cracks in the ground. Migrated tar is weathered into weathered black tar and eventually weathered particulate tar. This type of migration is usually stable at a slow speed and is capable of covering a large area over extended periods.

More detailed information of site visits is attached in Appendix II: Site Visit Reports.

According to the information gathered from the site visits. The nature of acid tars, especially those exposed to the environment, had changed since they were disposed of decades ago. Due to the pressure of capping layers and self weight, acid tars do not remain stable in a lagoon. Migration problems were found in most sites along various pathways. At non-capped acid tar lagoons, a layer of top water was usually found because of precipitation and the impermeability of acid tars. The top water was acidic, rich in sulfate. It also seems to deposit a thin black organic coating on the edge of the lagoons. Weathering appears to be relatively complex with several different forms present. Such observations lead to further questions and issues not dealt with in the literature and to be addressed as part of the main objectives.

Chapter 4 Literature Review: Sulfur Chemistry, Leaching Tests, NAPL Fingering and Instrumental Analysis

4.1 Sulfur Chemistry

4.1.1 Sulfur

Sulfur is a p-block element in group VI immediately below oxygen and between phosphorus and chlorine. It is the sixteenth element in abundance on earth. Elemental sulfur exists in native form, as a crystalline yellow sulfur consisting of S_8 molecules in which the sulfur forms strong bonds to itself. In nature, sulfur can be found as a pure element or as sulfide and sulfate minerals. It is also an essential component of all living cells. There are three main commercial sources of sulfur: (i) elemental sulfur in the caprock salt domes in the USA and Mexico, and the sedimentary evaporite deposits in southeastern Poland; (ii) H_2S in natural gas and crude oil, and organosulfur compounds in tar sands, oil shales and coal; (iii) pyrites (FeS_2) and other metal sulfide minerals (Greenwood and Earnshaw, 1997).

Sulfur is a very reactive element especially at slightly elevated temperature. The ignition temperature of sulfur in air is 250-260°C. Sulfur can occur in at least five oxidation states: -2 (sulfide, H_2S and organosulfur compounds), -1 (disulfides, S_2^{2-}), 0 (elemental S), +4 (SO_2) and +6 (sulfates). It can be found in both inorganic and organic compounds. Table 4-1 lists common inorganic and organic compounds of sulfur.

Sulfur compounds	**Description**
Inorganic sulfur compounds	
Sulfide S^{2-}	for example, cadmium sulfide (CdS)
Sulfites SO_3^{2-}	Salt of sulfurous acid, generated when SO_2 is dissolved in water
Sulfate SO_4^{2-}	Salt of sulfuric acid, generated when SO_3 is dissolved in water
Thiosulfate $S_2O_3^{2-}$	Ammonium triosulfate used in leaching gold.
Polythionic acids ($H_2S_nO_6$)	*n* can range from 3 to 80.
Sodium polysulfides	Na_2S_x
Sulfur hexafluoride, SF_6,	a dense gas at ambient conditions, is used as nonreactive and nontoxic propellant
Sulfur nitrides	chain and cyclic compounds containing only S and N
Thiocyanates	Compounds containing the SCN^- group
Organic sulfur compounds	
Thiols	(also known as mercaptans) have the form R-SH. These are the sulfur equivalents of alcohols
Thioethers (or sulfide)	have the form *R*-S-*R′*. These compounds are the sulfur equivalents of ethers
Sulfonium ions	have the formula RR'S-'R''', i.e. where three groups are attached to the cationic sulfur center.
Sulfoxides	have the form *R*-S(=O)-*R′*.
Sulfones	have the form *R*-S(=O)₂-*R′*.
Disulfide	Have the form of R-S-S-R'

Table 4-1 common sulfur compounds (Grenwood and Earnshaw, 1997. Carey, 2001).

R and R' referred to organic function groups, e.g. aliphatic, cyclic or aromatic

4.1.2 Inorganic sulfur compounds related to acid tars

As described in Chapter 2, acid tars are produced when washing crude organic mixtures by concentrated sulfuric acid. It is also reported that acid tars can release sulfur dioxide when exposed to the atmosphere. Therefore, sulfur dioxide, sulfur trioxide and sulfuric acid are the most relevant inorganic sulfur compounds to acid tars. These will be further discussed in this section.

Sulfur has many forms of oxides, for example S_2O, S_nO (n=6-10) etc. The most important and stable oxides of sulfur are SO_2 and SO_3. Sulfur dioxide is manufactured on a large scale by burning sulfur or H_2S, by roasting sulfide ores, or reducing $CaSO_4$. The physical properties of sulfur dioxide and sulfur trioxide are listed in Table 4-2. Sulfur dioxide has a molecular structure of O=S=O, in contrast to the bond order of 1.5 for the O-O bonds in O_3. Below 263K, in its liquid form , sulfur dioxide is a good solvent for organic compounds, e.g. alcohols, carboxylic acids, esters. Therefore, sulfur dioxide can effectively mix in acid tars and form a relatively stable structure if not disturbed or heated. In aqueous solution, sulfur dioxide is converted to only a small extent to sulfurous acid (HSO_3^- pKa=1.81, SO_3^{2-} pKa=6.97) and an aqueous solution of H_2SO_3 contains significant amounts of SO_2. An aqueous solution of sulfur dioxide can be oxidized to sulfate by many oxidizing agents, while sulfate can be reduced to SO_2 by a very high concentration of H^+.

Property	SO_2	SO_3
Physical appearance and general characteristics	Colorless, dense gas; pungent smell	Volatile white solid, or a liquid
Melting point (K)	198	290
Boiling point (K)	263	318
ΔH°(bp) (kJ/mol)	24.9	40.7

Table 4-2 physical properties of SO_2 and SO_3 at 293K and 1 atmosphere pressure (Housecroft and Sharpe, 2001)

SO_2 can be slowly oxidized to SO_3 by atmospheric O_2 in natural conditions though can be catalyzed by V_2O_5. The latter process is the first step of manufacture of sulfuric acid. Table 4-2 lists the physical properties of sulfur trioxide. Sulfur trioxide is very reactive and reacts vigorously and exothermically with water, forming a thick mist of sulfuric acid.

Depending on the oxidation state of sulfur and other conditions, sulfur has various forms of oxoacids, such as dithionous acid ($H_2S_2O_4$), Dithionic acid ($H_2S_2O_6$), sulfurous acid (H_2SO_3), disulfurous acids ($H_2S_2O_5$) and sulfuric acid (H_2SO_4). Sulfurous acid and disulfurous acid have never been isolated as a free acid and usually exist together in an equilibrium. The salts containing the sulfite ion [SO_3^{2-}] are well established and are good reducing agents, which are commonly used as wine preservatives.

Sulfuric acid is an enormously important industrial chemical and approximately 80% of commercially processed elemental sulfur is transformed into sulfuric acid. Sulfuric acid is principally used in the manufacture of fertilizers, metal mining and processing. It is also 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, generating acid tars in the process.

Sulfuric acid is a strong mineral acid. It is soluble in water at all concentrations. Sulfuric acid has many applications, and is produced in greater amounts than any other chemical besides water. 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. Fuming sulfuric acid (oleum), another form of sulfuric acid used in the production, as mentioned in Section 2.1.1, is a solution of sulfur trioxide in sulfuric acid and has an empirical formula $H_2S_2O_7$ (Senning, 1972).

Anhydrous H_2SO_4 is a very polar liquid. This is due to the fact that it can dissociate by protonating itself:

$$2\ H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

This allows protons to be highly mobile in H_2SO_4. It also makes sulfuric acid an excellent solvent for many reactions.

The hydration reaction of sulfuric acid is a two step reaction and is highly exothermic. The reaction forms hydronium ions, as follows:

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-,\ (pKa\ -3.0)$$

and then

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}.\ (pKa\ 1.9)$$

Sulfuric acid is one of the most important components of acid tars and 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. Some of the organosulfur chemical reactions involving sulfuric acid are discussed in the following section and its role in the chemistry of acid tars is further proposed in Section 4.1.4.

4.1.3 Organosulfur chemistry

The organic chemistry of sulfur is even more complex than its inorganic chemistry. The S atom in the ground state has the electronic configuration of 2,8,6 in electron shell No.1,2,3 and $3s^2 3p^4$ in shell No.3 with 2 unpaired p electrons. Therefore, the reactivity of sulfur is much more complex than oxygen which is immediately above it in the periodic table. If compared with oxygen, sulfur is much less electronegative than oxygen and in fact it has the same electronegativity as carbon. Therefore, the C-S bond is not polarized and is reasonably strong, though not as strong as C-O bonds. The oxidation states of organosulfur are II, IV, or VI with coordination number from 0 to 7. Table 4-3 lists a selection of compounds.

Oxidation State	S (II)			S(IV)		S(VI)		
Coordination number	0	1	2	3	4	4	6	7
example	S^{2-}	RS^-	R_2S	$R_2S=O$	SF_4	R_2SO_2	SF_6	SF_7^-

Table 4-3 compounds of sulfur

Due to its complexity, sulfur shows surprising versatility in function. Organosulfur compounds are usually good nucleophile and electrophiles. They can stabilize both anions and cations on adjacent carbon atoms. Important reactions include the S_N2 reaction, sulfonation, addition of sulfuric acid to alkenes, oxidation of thiols, and reactions of sulfonium salts, which are discussed below:

i) S_N2 reaction

S_N2 reaction is also known as bimolecular substitution nucleophilic, where a lone pair from a nucleophile (a reagent that forms a chemical bond to its reaction partner by donating both bonding electrons) attacks an electron deficient electrophilic center (a reagent attracted to electrons by accepting an electron pair in order to bond to a nucleophile) and bonds to it, expelling another group called a leaving group. Organosulfur compounds can be included as both nucleophile and leaving group in the S_N2 reaction, which is illustrated by Figure 4-1 (Clayden *et al.* 2006).

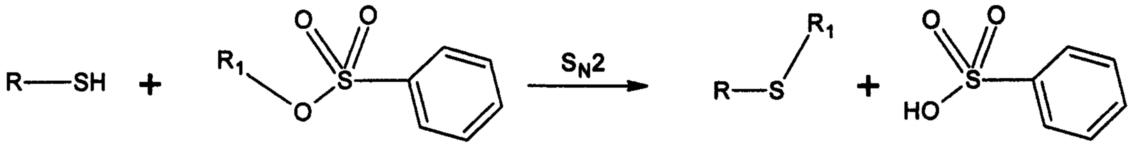


Figure 4-1 S_N2 reaction

ii) Sulfonation

Sulfonation is an electrophilic substitution reaction, where sulfuric acid attacks a hydrocarbon and produces sulfonic acid and water. An example of such reaction is the sulfonation of benzene, which is shown by Figure 4-2.

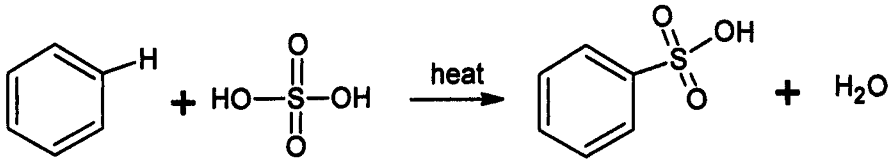


Figure 4-2 Sulfonation of Benzene

The above reaction is reversible but can be driven to completion by several techniques, e.g. removal of the water generated. Among the various electrophilic species present in concentrated sulfuric acid, sulfur trioxide is probably the actual electrophile in the sulfonation. Sulfonation by sufur trioxide is much faster and the equilibrium is displaced almost entirely to the product side (Carey, 2001). This is the reason why industrial processes commonly use 98.3% concentrated sulfuric acid or fuming sulfuric acid as reagent, as in the production of sulfuric acid.

iii) Addition of sulfuric acid to alkenes

The unsaturated bond, e.g. C=C in alkenes, can be attacked by sulfuric acid, which also generates organic sulfate (Figure 4-3). The addition of sulfuric acid to alkenes is the mechanism of removal of unsaturated hydrocarbon by sulfuric acid in acid tar production processes, which the attached alkenes will transform into sulfonic acids and dissolved in the sulfuric acid. The sulfonic acids are heavier than original hydrocarbon and therefore settled in the bottom of the reaction tank to form acid tars. Such reactions can proceed in a relatively low concentration of sulfuric acid (50% sulfuric acid).

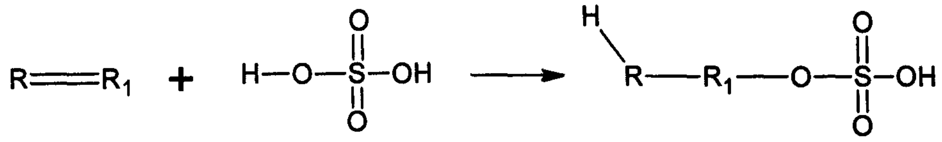


Figure 4-3 Addition of sulfuric acid to alkenes

iv) Oxidation of thiols

Thiols (R-S-H) are the sulfur analogs of alcohols (R-O-H). The most obvious property of thiols is their foul odour. Ethanethiol is added to natural gas so that leak can be detected without special equipment. The odour of thiols weakens with the number of carbons, because both the volatility and the sulfur content decrease. Compared to alcohols, the S-H bond of thiols is less polar than the O-H bond and the hydrogen bonding is much weaker than that of alcohols. Thiols are weak acids but are far more acidic than alcohols. The significant difference is that a thiol can be quantitatively converted to its conjugate base (RS^-) called an alkanethiolate anion.

Another major difference between thiols and alcohols concerns their oxidation reactions. Unlike the oxidation of alcohols which generate compounds with carbonyl groups, analogous oxidation of thiols to compounds with C=S functions does not occur and only sulfur is oxidized. The products include a series of acids containing sulfur in various oxidation states classified as sulfenic, sulfinic and sulfonic acids according to the number of oxygens attached to sulfur (Carey, 2001). The reaction series are summarized in Figure 4-4:

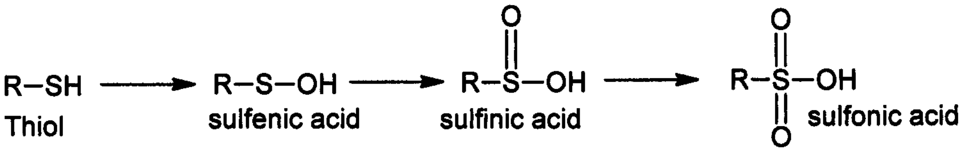


Figure 4-4 Oxidation of thiols

There are many other inorganic or organic sulfur compounds and reactions which are less related to acid tars and are beyond the scope of the thesis. The chemistry discussed in Section 4.1.2 and Section 4.1.3 is not necessary directly related to the chemistry of acid tars but may help to understand the chemical processes happening within acid tar lagoons. The following section proposes possible chemical processes reported in the literature which may be involved in acid tar lagoons.

v) Sulfonium salts

Sulfides are nucleophiles even when not deprotonated and the sulfur atom will attack alkyl halides to form sulfonium salts. The most important chemistry of sulfonium salts is based on their two attributes:

a) Sulfonium salts are electrophiles: nucleophilic substitution displaces a neutral sulfide leaving group.
b) The positive charge carried by the sulfur atom means that the protons next to the sulfur atom in a sulfonium salt are significantly more acidic than those in a sulfide, and can be deprotonated to give sulfonium ylids

(Clayden *et al.* 2006).

The reactions of sulfonium salts can be best described by Figure 4-5:

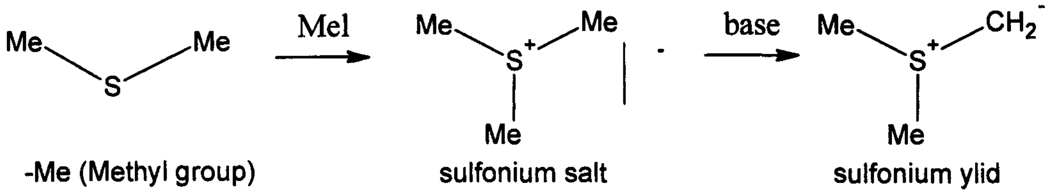


Figure 4-5 Reactions of sulfonium salts

4.1.4 Sulfur chemistry of acid tar lagoons.

The sulfur content of acid tars is partly contributed by sulfuric acid and partly by the naturally occurring sulfur compounds contained in the raw material. As listed in Table 4-1, there are many species of sulfur compounds, especially organosulfur compounds. Direct information of sulfur compounds in the raw material of the three acid tar production processes is limited. However, within a broader context, there are studies of naturally occurring sulfur compounds in related materials, e.g. coal, asphaltenes, crude oils etc.

Vairavamurthy A. *et al* (1994) reported that the sulfur compounds found in marine sediments include polysulfide, disulfide, thiophenic, sulfoxide, sulfonate and sulfate. Geraldine *et al* (1999) investigated the forms of sulfur compounds in asphaltenes and the dominant forms of sulfur are dibenzothiophenes. They further divided the sulfur compounds into two groups: a less oxidized group consisting of disulfides, alkyl and aryl sulfides, and sulfoxides; and an oxidized group consisting of more sulfoxides, sulfones, sulfonates and sulfates. Table 4-4 lists the major sulfur species identified by Geraldine *et al* (1999).

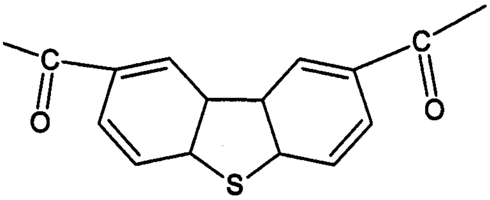
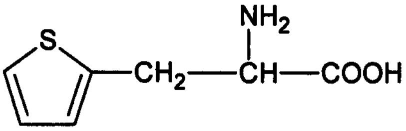
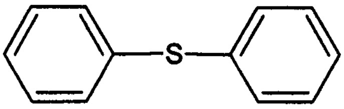
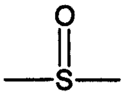
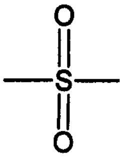
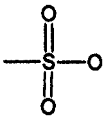
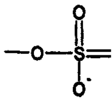
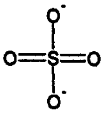
Forms of sulfur	Structure
Disulfide	C-S-S-C
Sulfide	C-S-C
Tilorone analog	
3-(2-thienyl)-DL-alanine	
Poly(phenylene sulfide)	
Sulfoxide	
Sulfone	
Sulfonic acid, sodium salt	
Dedecyl sulfate	
Sodium sulfate	

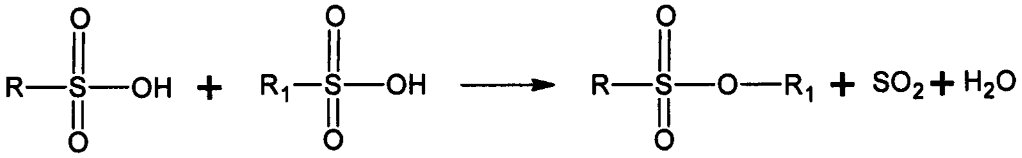
Table 4-4 Forms of sulfur in asphaltenes (Geraldine *et al*, 1999)

In coal, the inorganic species of sulfur are mostly pyrite (FeS_2) or marcasite (FeS_2, but lighter and more brittle) while the organic sulfur usually exists as mercaptans (RSH), aliphatic and aryl sulfides (RSR'), disulfides (RSSR') and thiophenes (Calkins, 1994). The organosulfur compounds in coal are mainly less oxidized. Xu and Kumagai (2003) studied the sulfur transformation during the coal pyrolysis processes and conclude that the inorganic sulfur will be fixed into organic sulfur or be released as H_2S gas. This is highly dependent on temperature (the fixing processes mainly occur at intermediate temperatures while higher temperature usually lead to more H_2S) and the organic sulfur can be transformed into a more oxidized state depending on the carrier gas and temperature. Therefore, crude benzole, a by-product of the coal carbonization process and one of the raw materials that produce acid tars, would be expected to have the organosulfur compounds above, especially more oxidized organosulfur group, and be dissolved into acid tars by concentrated sulfuric acid. If combusted in the air, the end product could be a mixture of gaseous SO, SO_2, SO_3, HSO_2, HSO_3, and H_2SO_4 aerosols and the dominant product would be SO_2 (Savel'ev A. M. *et al.* 2002). Such circumstances should not be expected in the acid tar production process. However, if applying incineration as a source removal technique for acid tar lagoons, the gas emission problem must be considered for the above gaseous sulfur compounds.

Based on the information discussed in above sections, it can be concluded that the sulfur containing compounds of acid tars are very complex. The inorganic species of acid tars include sulfuric acid, sulfur trioxide, inorganic sulfate and possibly dissolved sulfur dioxide. The organic species of acid tars may be sulfides, disulfides, sulfoxides, sulfone, sulfonic acid, organic sulfate and many other relative ionized salts and minor species. It should be noted that some of these sulfur forms may not have an isolated state and acid tars are likely to contain many organosulfur compounds that form a very complex equilibrium state, which in turn will vary depending on the environmental conditions. The most important reactions of acid tars regarding their sulfur chemistry have been reported and are listed below.

i) Sulfonation and addition of sulfuric acid to alkenes which generate sulfonic acids and organic sulfate, as described in Section 4.1.3.

ii) Sulfonic acids can be decomposed and release sulfur dioxides when heated or disturbed (Bukharkina *et al*, 1993). This is the reverse reaction of sulfonation and is postulated to be the main source of sulfur dioxide emission problems encountered in most acid tar lagoons.



$$R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH + R_1-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \longrightarrow R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-R_1 + SO_2 + H_2O$$

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

iii) Sulfuric acid is also capable of releasing sulfur dioxide by reaction with hydrocarbons under heated conditions (Zharkikh *et al*, 1994).

$$R-H + R_1-H + H_2SO_4 \longrightarrow R-R_1 + 2H_2O + SO_2$$

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

Furthermore, the sulfuric acid and complex organosulfur compounds in acid tars will alter the characteristics of acid tars. They will make acid tars more hydrophilic and therefore increasing the leaching ability of acid tars.

4.2 Bitumen and Other Organic Mixtures similar to Acid Tars

4.2.1 Overview

As a relatively new research area, the bibliography of acid tars is very limited, which in turn limits direct understanding of acid tar behaviour. However, there are several similar organic materials that originate from oil or coal carbonization processes, such as bitumen, asphaltene, coal tar etc. By drawing upon previous experience on the composition, properties and behaviors of such materials in the literature, valuable information of acid tars can be inferred.

4.2.2 Origin

Viscous, complex organic mixtures similar to acid tars are generally produced from two processes, coal carbonization or oil-refining.

Coal carbonization is mainly used to produce coke or coal gas for industrial and domestic use. Coal tar is the waste residue of the coal carbonization process and is a viscous, black liquid with the smell of aromatic hydrocarbons. It is a complex and variable mixture of phenols, PAHs, and heterocyclic compounds. The condensed liquid from cooled coal gas is crude benzole, which was further refined as motor fuel and was one of the raw materials that produced acid tars (Claxton, 1961).

The materials involved in the petrochemical industry are much more complex. The naturally occurring raw material of the industry is petroleum or crude oil, a complex organic mixture of mainly alkenes of various lengths. The approximate length range is C_5H_{12} to $C_{18}H_{38}$. Any shorter hydrocarbons are considered as natural gas. Crude oil is usually black or dark brown colored but varies greatly in appearance depending on composition. Crude oil is usually found in porous rock formations in the upper strata of some areas of the Earth's crust and can be pumped out by drilling wells. Extremely heavy crude oil is usually mixed with sand, clay and water, and is commonly referred to as tar sand or bituminous sand (Speight, 1980).

The oil refining process mainly involves fractional distillation of crude oil which produces various fractions depending on their boiling point. The major fractions from top to bottom of the distillation plant are gasoline (petrol), kerosene, diesel oil, fuel oil and bitumen. Bitumen is the heaviest residual (bottom) fraction and the one with the highest boiling point, boiling at approximately 525 degrees Celsius. Bitumen is a mixture of organic liquids that are highly viscous, black, sticky, and composed primarily of highly condensed polycyclic aromatic hydrocarbons. Most bitumens contain sulfur, several heavy metals, and other toxic elements. Bitumen is primarily used for paving roads. Its other uses are for general waterproofing products, including the use of bitumen in the production of roofing felt and for sealing flat roofs. Asphaltene is similar to bitumen, but composed of lighter compounds. The most apparent feature of asphaltene is that it contains primarily

NSO-compounds (organic compounds containing nitrogen, sulfur and oxygen), which makes it more polar than the other materials discussed above and similar to acid tars which also contain large potion of polar organic compounds.

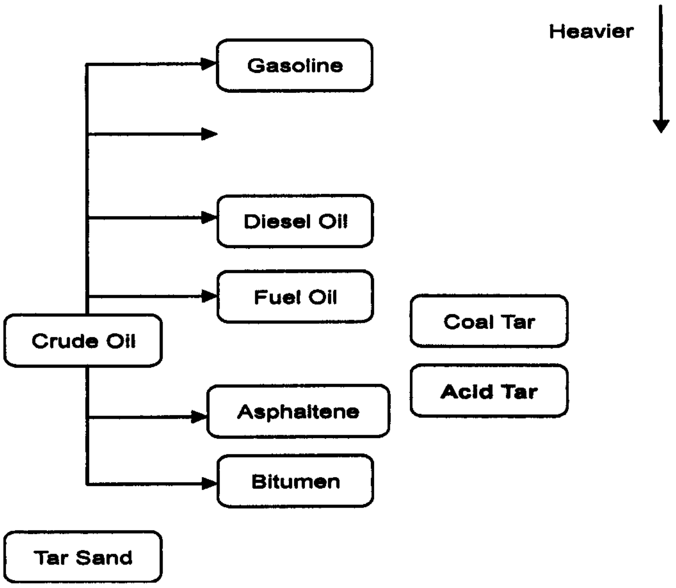


Figure 4-1 relationships of various organic mixtures

Figure 4-1 shows the relationship of the discussed organic materials with respect to their average molecular weight.

4.2.3 Chemical Composition and Physical Properties

Similar to acid tars, the composition of bitumen, coal tar or asphaltenes are highly heterogeneous depending on their origin and the processes involved in their production. A representative quantitative composition is not available for these materials. The discussion of their composition will, therefore, focus on the comparison of organic compounds contained which should be inferred from their properties or behaviours in the environment.

Baginska and Gawel (2003) reported the chemical composition of bitumens produced from Venezuelan and Uralian crude oils and the effect of production technology on the composition. Bitumen is considered to contain four groups of organic compounds: saturated hydrocarbons, naphthene-aromatics, polar-aromatics and asphaltenes. The authors concluded that the generic composition of bitumen is influenced primarily by the technology of production while the composition is also affected by the chemical type of the original crude oil. The research also indicated that the bitumens produced by intensive air-blow technique, where hot oxidizing gas (air) is blown through crude oil for a period of time to alter its thermal maturity (hydrocarbon content), usually contain heavier asphaltenes. Hwang. *et al* (1998) reported the chemical composition of solid bitumen samples from Zaire using the same categories and indicated that the NSO compounds and asphaltenes comprised approximately 55% of the sample weight. Subramanian and Hanson (1998) analyzed 4 bitumen samples extracted from the Utah oil sands. The components with boiling point <811K compromised 40.9-53.5% of sample weight, the molecular weight was 426 to 570 and the asphaltene content ranged from 2.9-23.6%.

Gurgey *et al (*2007) analyzed bitumen samples collected from western Turkey and found the bitumen is composed primarily of polar NSO compounds and asphaltenes (77%). Other components include n-alkanes (n-C_{19} to n-C_{38}) and unresolved complex mixture (UCM). Such a composition indicated that the bitumen has been moderately altered by the hot geothermal waters that accompanied it.

Zhao *et al* (2002) analyzed the composition of bitumen samples when studying the refinery processes of extracting bitumen from oil sands, which is an alternative source of crude oil when the lighter, liquid form of crude oil is diminishing. The average molecular weight of this bitumen was within the 800-1100 range. The total sulfur content was 4.3-7.4% percentage weight and the dominant sulfur compounds were the thiophenic species which represented 60% of the total sulfur.

There are other studies that describe the composition of bitumen using other categorized systems depending on the aims of the study and analytical methods applied. However, the general consensus is that the primary compositional groups of bitumen are asphaltenes, aromatics, and saturated hydrocarbons.

Coal tar differs from acid tars in that it compromises mainly non-polar alkanes. Alcaniz-Monge *et al.* (2001) reported the elemental composition of several coal tar samples and that the weight percentage carbon ranged from 91% to 93%, while the NSO contents were 2%-3%.

The asphaltenes contain primarily carbon, hydrogen, nitrogen, oxygen and sulfur with trace amount of vanadium and nichel. The C:H ratio is approximately 1:1.2 and the average molecular weight is in the range of 400 and 1500 depending on the source (Mullins, 2007). It is the most polar group of bitumen which contains most of bitumen's NSO compounds.

The appearance and odour of bitumen, coal tar and asphaltenes are similar to those of acid tars. They are viscous, black or dark brown colored semi-liquids with the odour of aromatic hydrocarbons. They are therefore difficult to distinguish purely based on their appearance. The pH of bitumen is generally acidic due to the carboxylic acids they contain. Coal tar also contains phenolic and carboxylic acids, commonly described as tar acids, which are also acidic (Zhang *et al*, 2006). The viscous nature of bitumen is principally attributed to the internally suspended asphaltene particles and is further influenced by the carboxylic acid content. It can be considered as colloidal system in which micelles of high-molecular-weight organics (asphaltenes) are dispersed in an oily phase (maltenes) consisting of low-molecular weight saturated and aromatic hydrocarbons together with resins (Jimenez-Mateos *et al*, 1996). Bukka et al, 1994 suggested that bitumen with higher viscosity usually contained higher carboxylic acid content.

The most distinct compositional differences between acid tars and bitumen is the high sulfuric acid content and high level of sulfur containing compounds in acid tars. The sulfuric acid and sulfonic acid not only makes acid tars more acidic, but also renders them hydrophilic because of the soluble organosulfur acids and organosulfur ions, as introduced in section 4.1.4. Therefore, the water content of acid tars could be as high as 50%, as described in Section 2.2.2, which enhances the leachability of acid tars and can have significant impact on the environmental behaviour of acid tars.

4.2.4 Leaching & Weathering Behaviour

The environmental behavior of bitumen and other organic mixtures, such as leaching and weathering, may provide useful insight into similar processes occurring in acid tars, though the significant differences between the materials should not be ignored.

One of the major parameters that determines the leaching behavior of bitumen is its aqueous soluble components. One group of the water soluble components of bitumen is carboxylic acids and their salts. Vandegrift *et al.* (1980) analyzed the carboxylic acids in oil shale bitumen sampled from the Green River in the US and found that the main species of carboxylic acids were long chain aliphatic carboxylic acids with carbon numbers in the range of 21-38 and their salts with Fe and Mg, which could be leached into the aqueous phase.

Another important group of compounds in bitumen is PAHs. They are less soluble in water but pose significant environmental threat. Bitumen is commonly mixed with sand and gravel (asphalt) to coat the roads, roofs and to line water retaining cisterns and pipes. Brandt and De Groot (2001) studied the leaching behavior of PAHs from 9 bitumen samples and 1 asphalt sample made from one of the bitumens. A series of 30 hour dynamic leaching tests with a liquid solid ratio of 10:1 and static leaching tests (cascade leaching tests) with fixed liquid solid ratio 4.5:1 (the leachate is refreshed after 0.25, 1, 2.25, 4, 9, 16 and 36 days) were performed using pH 4 acidified water. The results from both static and dynamic leaching tests indicated that the PAH concentration in the leachate remained well below the surface water limits. In the static leaching tests, the concentration of PAHs increased in the first day and reached a steady state within 3-6 days, which implied that the leaching is controlled by kinetic processes. Previously, coal tar has also been used in many applications where now bitumen is applied. The leaching of PAHs of coal tar has also been studied. Munch (1992) reported the PAH concentration in coal tar based asphalt was ten times higher than those found in bitumen based asphalt, which indicates that the PAHs form more stable structures within bitumen than in the coal tar.

The weathering of bitumen exposed to the environment is primarily due to physical processes, oxidation and biodegradation. The end product has a very similar appearance to the weathered black tar observed in this research, as shown in Figure 4-2.

Littke *et al.* (1991) studied the effects of natural weathering on the chemical composition of bitumen based on geochemical data on Posidonia Shale (Early Toarcian) and found that the soluble organic matter and sulfur content was decreased due to the weathering, which may significantly add to anthropogenic pollution.

Figure 4-2 Surface weathered bitumen at a site in Turkey (Gurgey *et al*,(2007)

Saeed *et al.* (1998) assessed the impact of weathering on crude oil spills in Kuwait desert. The crude oil spills was resulting of the 1991 Gulf War and aftermath. The destruction of oil production, storage and refining facilities leaked massive oils and caused fires. Approximately 200 oil lakes were formed which contains 60 million barrels of oil. The composition of the various lakes depended on the source crude oils, degree of combustion, surface temperature and many other variables. The oil lakes were weathered in the hot climate of Kuwait (>50°C in summer) and thickened to semi-solid status. The compositional change of the weathered oil during the 1991-1996 period was analyzed. The results indicated that asphaltene, aromatic and resin contents of the oil from most of the lakes increased significantly as a result of loss of volatiles. The saturates (aliphatic compounds) decreased as weathering progressed correspondingly. The PAH content also increased due to the weathering. There are still heavily contaminated areas where untreated leftover oil was presented and the weathering process has continued. The weathering was considered to be primarily due to physical and chemical processes and biodegradation was not considered significant because of the extreme climatic conditions.

The leaching and weathering behaviors of bitumen and other organic mixtures are to certain extent similar to that of acid tars. However, the high sulfuric acid and sulfur containing organic contents of acid tars made them more mobile than bitumen. Acid tars have more water soluble components, which may significantly enhance their leaching ability. The high sulfur content of acid tars may have impact on its weathering process and their mobility.

4.3 NAPL Fingering

To some extent acid tars can be considered as a Non Aqeuous Phase Liquid (NAPL). Thus it is of interest to briefly review the migration phenomena associated with NAPLs. The mechanism of gravity driven fingering migration of two immiscible fluids, such as the fingering of water/air in an initially dry, water-wettable coarse media has been studied by many authors. Glass and Nicholl (1996) summarized the physics of fingering and reported that such a behavior is the result of the interplay of gravitational, viscous and capillary forces. The fingering process is influenced by a number of conditions, such as uniform or non-uniform initial moisture content, media heterogeneity and the existence of large void spaces, e.g. macropores and fractures. It is also observed that the fingering flow often create a heterogeneous permeability field such that subsequent events follow preferential flow paths defined by previous fingers.

Non-aqueous phase liquids (NAPLs) that were spilled or leaked into the subsurface pose environmental problems at many sites. The primary concern at these sites is not the NAPL itself but the dissolved aqueous phase contaminant plume it generates. The plume generated by NAPLs sometimes develops preferential dissolution pathways in water saturated porous media and can be explained by the similar mechanism of the fingering of two immiscible fluids, which in this case is NAPL and water (Imhoff *et al*, 2003). However, there is a key difference between water/air and NAPL/water systems in that water is usually the natural wetting fluid in unsaturated porous media to air while NAPLs is the non-wetting fluid to water. Zhang and Smith, 2002 reported that the fingering process of NAPLs can be divided into two stages, fingering initiation stage and the finger elongation stage. At the finger initiation stage, many protuberances developed at the water/NAPLs interface. At the finger elongation stage, some relatively large protuberances appeared at the finger initiation stage developed to primary fingers and secondary fingers may develop on the existing primary fingers. The fingers continued growing downwardly in a winding manner.

4.4 Leaching Tests

The standard UK leaching test recommended by the British Standard: BSEN12457-2 :2002 Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction). BSEN12457 is designed for contaminated soil and waste material, which is not entirely suitable for bulk impermeable acid tar samples. The major revision to BSEN12457 is particle size analysis and agitation. BSEN12457 requires a test sieving particle distribution analysis on the sample, which is not applicabble to acid tars samples. The aim of agitation suggested by BSEN12457 is to achieve maximum separation of soil and contaminants. In the case of acid tar, however, acid tar itself is the carrier of contaminants so such intensive agitation is not necessary. Hansen *et al* (2004) raised issues of the batch leaching test of non-volatile organic compounds: (i) artificially generated organic colloids may result in an overestimated concentration of contaminants; (ii) an unexplainable underestimated small PAH (2-3 rings) concentration when compare batch leaching test results with equilibrium column leaching test in some cases. The aim of this PhD research is to investigate the leaching behavior of acid tars, including all forms of mobile components in aqueous phase, such as water soluble components and organic colloids. Batch leaching tests, therefore, are regarded as a useful measure of leaching behavior of acid tars.

Kim and Osako (2003) reported that the leaching of PAHs contaminated soil is positively influenced by shaking time, temperature, negatively influenced by ionic strength, and not influenced by liquid-to-solid ratio and pH level. The results refer to dissolved contaminants and PAHs only. However, it provides useful information for leaching tests of organic compounds, such as acid tars. Shaking time and temperature can be controlled at same level for all tests. However, ionic strength in different batches can be highly variable depending on sample properties. Some of the contaminants of acid tars may not be mobile under low liquid-to-solid ratios because of the high ionic strength of sulfate. There are also equilibrium and diffusion issues that prevent all mobile components from getting out of acid tar samples at one single batch. Cascade leaching tests, therefore, are advantageous in these circumstances.

Cascade leaching tests are staged series of batch tests that achieve a high liquid-to-solid ratio. Fytianos *et al* 1998 reported cascade tests of L/S ratio 5 to 100 on flyash, however no literature was found on cascade tests of an organic mixture such as acid tars. A cascade test provides useful information on acid tars such as longer term leaching and total leaching capacity (taking colloids into account). In this PhD study, the cascade leaching test procedure is adapted from the contaminated soil leaching test used by Czerewko *et al* (2001), which used a 5 stage extraction (cumulative liquid to solid ratio 100) to study the leaching behavior of heavy metals, metalloids and anions in casting foundry sands, metal smelting slags and colliery spoil.

An equilibrium column leaching test, which water is flow through a layer of permeable material and the level of contaminants in the leachate is determined by the equilibrium of contaminant concentration in the solid material and in the aqueous phase, is the method recommended for studying the leaching behavior of non-volatile organic contaminated soil (Hansen *et al*, 2004). The recommendation is based on a number of advantages that column leaching tests have, including (i) no additional treatment of the eluate (e.g. filtration) needed after leaching; (ii) the test material is treated very gently during testing and no grinding of the material is required; and (iii) the results are reproducible. However, column leaching tests are not directly applicable to acid tar because of its viscous nature and low permeability which will result in clogging of the leaching column. Modification of the method will be required.

4.5 Instrumental Analysis

4.5.1 Inorganic Analysis

Inorganic analysis of acid tars and the leachate from leaching tests is in principle fairly straight forward. Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) and Ion-exchange Chromatography (IC) are used as instrumental techniques for inorganic analysis.

ICP-AES is a type of emission spectroscopy that uses inductively coupled plasma to produce excited atoms that emit electromagnetic radiation at a wavelength characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample (Skoog *et al,* 1992). It is commonly used to determine heavy metals (Feng *et a,l* 2007) or inorganic elements, such as arsenic in environmental samples. ICP-AES is applied in this research to analyze the elemental composition of various forms of solid acid tar samples. The actual ICP-AES analysis was performed by Sheffield University Assay Office and the sample was prepared in the lab by ashing and acid digestion. Detailed sample preparation procedure is listed below:

a) Weight 10 grams of acid tar samples and transfer into a ceramic plate.
b) Place the plate in an oven and heated at 720°C for 24 hours.
c) Add 3ml of concentrated nitric acid (69%) to the plate. Place the plate on an 80°C hotplate for 2 hours to digest.
d) Transfer the liquid to a 15ml container and add deionized water until 15ml.
e) A blank sample with same procedure describe above without acid tar is also prepared for comparison.
f) Send the 15ml sample for ICP-AES analysis.

The ICP analysis is a good screening technology to look for any potential hazardous elements in acid tars, e.g. heavy metals. However, it does not provide detailed information of inorganic species and the high temperature ashing process may cause the loss of some elements, e.g. mercury, gaseous sulfur etc. A detailed discussion of limitations of ICP-AES is presented in Chapter 8.

IC is a process that allows the separation of ions and polar molecules based on the charge properties of the molecules. It can be subdivided into cation exchange and anion exchange. It can be used as first step of protein purification, as well as for analyzing water samples for targeted cations and anions (Skoog *et al,* 1992). IC is used in this research to analyze inorganic contaminants in acid tar leachate. The acid tar leachate generated by leaching tests is prepared by filtering and dilution. A detailed procedure is listed below:

a) The leachates are filtered by a 0.45μm filter paper.

b) Depending on the pH and colour (an indication of its contamination level) of the leachates, it needs to be diluted for 10 to 50 times respectively.

c) Transfer the diluted leachate into IC sample valve and seal it with a filter cap.

d) A blank sample with same procedure describe above using deionized water is also prepared for comparison.

e) Place the valves into sample rack and feed it to the auto sampler of DIONEX DX 120 IC.

The DIONEX DX-120 IC used in this PhD has a conductivity detector. For cation detection, a 250mm IonPac CG12A is used as the guard column and a 4*250mm IonPac CG12A cation exchange column is used as the analysis column. The eluent for cation separation is 20mM methane sulfonic acid and the pH is buffered at 1.70. For anion detection, a 250mm IonPac AS14A is used as the guard column and a 4*250mm IonPac AS14A anion exchange column is used as the analysis column. The eluent for anion separation is 8mM Na_2CO_3 and 1.0 $NaHCO_3$ buffering solution and the buffered pH is 10.80.The IC analysis provides concentration of inorganic species dissolved in the leachate. However, the IC can only determine the anions and cations calibrated by the standard solution and the results could be influenced by the presence of complex sulfur containing organics. Limitation, repeatability and charge balance of IC analysis on acid tar leachates are further discussed in Chapter 8.

4.5.2 Organic Analysis

Acid tars are extremely complex organically with thousands of organic compounds, mostly heavy hydrocarbons which have been characterized to a very limited extent.

The organic analysis of acid tars will, therefore, mainly focus on potential hazardous contaminant groups and follows the standard analytical methods where available in the laboratory. As discussed in Section 2.2.2, the major potential organic contaminants of acid tars are BTEX, phenols, PAHs and sulfonic acids. Sulfonic acids are hazardous mainly because of the acidity and are a large group of organics out of which it would be very difficult to identify every single species, nor is it useful or economical. pH is a good and simple parameter to address their environmental risk together with that of sulfuric acid. The analytical methods for BTEX, phenols and PAHs are discussed below.

BTEX is a group of volatile organic hydrocarbons. In the New Dutch List threshold (optimum) concentration of BTEX is 0.2μg/L in groundwater and 0.05mg/kg (detection limit) in soil. The determination of BTEX in aqueous samples is usually carried out by gas chromatography with flame ionisation detection (GC–FID) and the samples are often prepared by liquid–liquid extraction with an appropriate organic solvent. Acid tar samples are mainly in solid or viscous liquid forms and are hard to handle during extraction. Static Headspace (HS) (Florez Menendez *et al,* 2000) is a suitable alternative sampling technique for acid tars.

Phenols are toxic aromatic compounds with hydroxyl group bonded with phenyl ring. They are slightly acidic and ICRCL 59/83 Trigger Concentrations set their threshold level at 5mg/kg in air-dried soil. Phenol analysis is covered by British Standard: BS 8855-2:2000 which use High Performance Liquid Chromatography (HPLC) as analytical instrument. The method can detect phenolic compounds of catechol, resorcinol, phenol, cresols (ortho-, meta-,para-), xylenols (2,3;2,4;2,5;2,6;3,4 and 3,5); 2-isopropylphenol, 1-naphthol and 2,3,5 trimethylphenol with a detection limit of 0.02 mg/kg to 10mg/kg if in contaminated soil.

PAHs are a group of aromatic hydrocarbons that are highly carcinogenic (certain species) and therefore highly hazardous to human health. Solid PAHs are most dangerous because their ability of rising as dust due to their crystals becoming electrostatically charged. The New Dutch List set threshold (optimum) level of total PAHs in soil sediment at 1mg/kg dry weight and action level at 40mg/kg dry weight. PAH analysis is covered by British Standard: DD 8855-1:1999 using Gas Chromatography – Mass Spectrometry (GC-MS) technique, which can determine 16 priority PAHs in extracted samples.

More detailed information of organic analysis of acid tar samples is discussed in Chapter 7.

4.5.3 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis *(TGA)* is a technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere is programmed (Haines, 1995). TGA is widely used in thermal behavior studies of coal tars in either air (Dou *et al,* 2001) or nitrogen (Lin *et al,* 2004) gas flow. Air gas flow is applied to simulate combustion of coal tar while nitrogen is applied as an inert carrier to study weight loss of an organic mixture based on their boiling points or decomposition temperature. Nitrogen gas flow can, therefore, provided more direct information on molecular weight distribution and is more suitable for the study of acid tar samples. Nesbit *et al,* (1995) suggested TGA as an analytical technique to study thermal behavior of acid tars.

Chapter 5 Monitored Natural Attenuation and Conceptual Model of Acid Tar Lagoons

5.1 Monitored Natural Attenuation

Natural Attenuation usually describes natural processes that reduce the mass, toxicity, mobility, volume and concentration of contaminants in soil or groundwater. Schirmer and Butler (2004) summarized the processes influencing fate of liquid organic contaminants, which are dissolution of the residual multi-component source; mass transfer of the dissolved organics to the groundwater; transport in the groundwater by advection, dispersion and diffusion; and chemical and biological transformations. They also pointed out that physical processes are usually incapable of reducing concentration of contaminants to give acceptable water quality standards and chemical and biological transformations are the only natural processes that are capable of permanently removing contaminant masses from the environment. Monitored Natural Attenuation (MNA), therefore, is a potential management strategy for contaminated land, but requires sound understanding of physical, chemical and biological processes and a well-designed monitoring system. The U.S. EPA Remedial Technology Fact Sheet 1999 summarizes components that are important for Natural Attenuation, as shown in Fig 5-1, which are biodegradation, sorption, dispersion and dilution, chemical reactions and volatilization (evaporation). It also divided the contamination into source (bulk fluid), smear zone and dispersion and dilution zones.

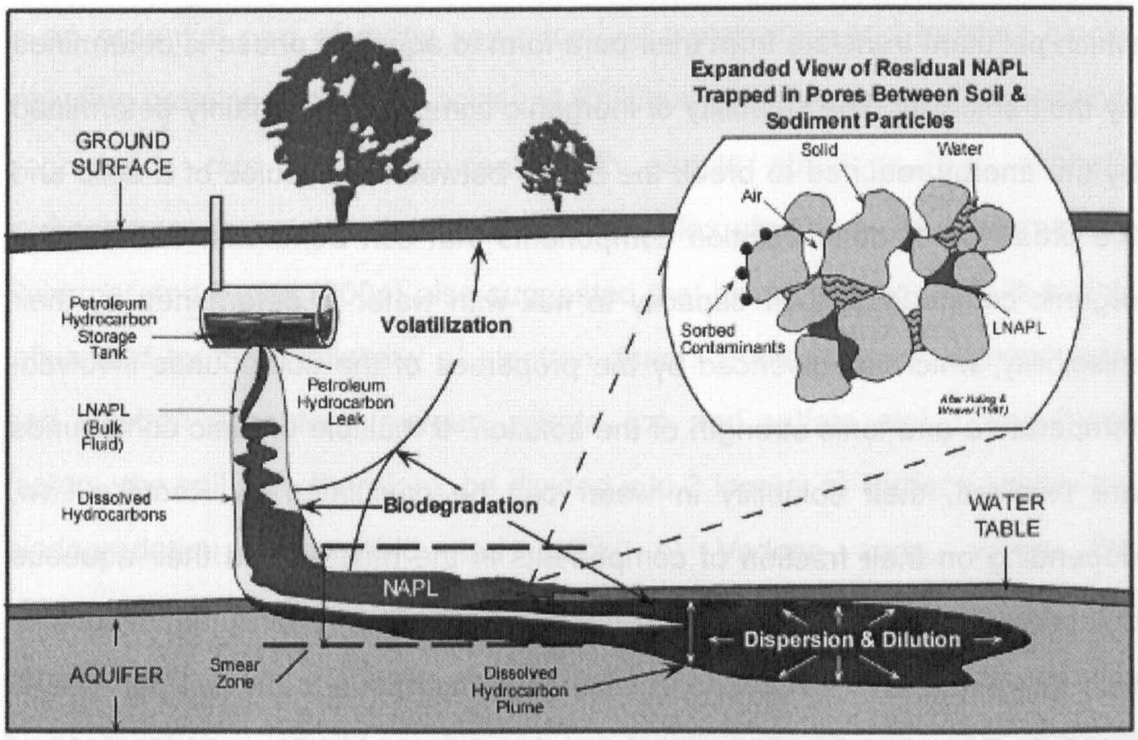


Figure 5-1 Components of Natural Attenuation (The U.S. EPA Remedial Technology Fact Sheet 1999)

Physical processes control the movement of contaminants in soil and groundwater. Many chemicals can move to groundwater because they can dissolve in soil water and move down to groundwater in solute form. Other chemicals, such as petroleum products, are less soluble in water. But still can be flushed into groundwater by the downward movement of water. The rate of transport is greatly depends on properties of particular chemicals, soil type, climate and vegetation. The mechanism of transport of contaminants in the groundwater is primarily controlled by a process called mass transport or convection, which refer to the passive movement of a dissolved chemical with water and can be determined by Darcy's law. In addition, contaminants may slowly redistribute within the soil pore water by molecular diffusion, which can be determined by Fick's Law of Diffusion. Furthermore, the velocity difference within an individual pore depending on the relative position with respect to the pore wall leads contaminants to mix, which is called mechanical dispersion (Hemond and Fechner, 1994).

Chemical processes that affect the fate and transport of contaminants in soil and groundwater are primarily dissolution and sorption. The extent to which pollutant transfers from their pure form to aqueous phase is determined by their solubility. The solubility of inorganic compounds is mainly determined by the energy required to break the bonds between molecules of a solid and the presence of other solution components that can bond with the ion. For organic compounds, their capacity to mix with water is determined by their miscibility, which is influenced by the properties of the compounds involved, temperature and ionic strength of the solution. If multiple organic compounds are involved, their solubility in water can be calculated by Raoult's Law, depending on their fraction of components in the mixture and their aqueous solubility. Sorption or retention describes the interaction of pollutant molecules with soil particles. The sorption of inorganic compounds on soil particles is primarily determined by ion exchange processes, where negatively charged soil particles attract positively charged inorganic ions. The sorption mechanism for organic contaminants should be considered in terms of polar organics and non-polar organics. The mechanism for polar or ionized organic compounds is similar to that of inorganic ions while the non-polar organics obeys a "like dissolves like" rule in which the non polar organic molecules prefer to associate with the soil organic matter because of their similar non-polarity (Pepper *et al,* 1996).

Biodegradation is the breakdown of organic compounds through microbial activities. It is a series of microbiological processes which ultimately result in the oxidation of the organic compounds. Complete biodegradation will oxidize the parent compounds into carbon dioxide and water that provide carbon and energy for growth and reproduction of cells, which commonly referred to as mineralization. Such degradation may not happen due to a number of limiting factors, which results in incomplete oxidation leaving smaller intermediate organic molecules. The limiting factors are: i) Oxygen deficiency, which commonly results in faster aerobic biodegradation and slower anaerobic biodegradation. ii) Type of microbial populations and organic matter content. iii) Availability of nitrogen, a macronutrient that limits microbial activity because it is an essential part of many key microbial metabolites and building blocks including proteins and amino acids. iv) Pollutant structure, generally speaking, degradation rate of contaminants with simple structure (e.g. aliphatic hydrocarbon) is quicker than it is with complex structures (e.g. aromatics). Schirmer and Butler (2004) also suggested that biodegradation rate is mainly influenced by the availability of electron donors (mainly organic compounds) and electron acceptors (oxygen, nitrate, ion and sulfate etc). Given these factors, the soil can, therefore, be divided into 3 layers: a) Surface, where the biodegradation is aerobic and quick; b) Vadose zone, where the biodegradation is also aerobic but acclimation times may be necessary for microbe population to build up; and c) groundwater region, where the biodegradation is initially aerobic and can rapidly become anaerobic owing to insufficient oxygen (Pepper *et al,* 1996). Among the three processes, microbiological processes are the most important factors of Natural Attenuation because biodegradation metabolizes organic compounds as carbon source and therefore permanently removes them from the environment.

The evaluation of MNA as an option for contaminated land management includes understanding of how the processes described above influence the transportation of contaminants offsite (scale of the plume, estimated concentrations and timescale of the leaching etc) and the design of the monitoring system (selection of monitoring parameters, allocation of monitoring wells and sampling techniques).

Studies of Natural Attenuation of petroleum hydrocarbons, coal tars and other organic hydrocarbons at former spill sites have been widely reported. The organic compounds are usually present as non-aqueous phase liquid (NAPL) and the mobility in the groundwater depends on their solubility as well as geological and geochemical characteristics of the sites (Eberhardt and Grathwohl, 2002). King and Barker 1999 also concluded that compounds from the same source can display distinctly different patterns of plume development and mass transformation was a major influence on plume behavior for all observed compounds. It should be noted that the most active region of the Natural Attenuation process is the dispersion and dilution zone, where the level of contamination is low enough for microbes to act.

Although being a valuable remediation options, Natural Attenuation is a long-term process, with a usual timescale of to decades or centuries. From experimental results, Eberhardt and Grathwohl (2002) concluded that the timescales for Natural Attenuation of a 0.5m coal tar contaminated blob would be weeks for BTEX and decades for the PAHs. Williams *et al,* (2001) also reported that at a 50 years old phenol acidified coal tar site, the half-life of sulfate reduction was about 15 years and it took over 30 years to achieve 18% Dissolved Organic Carbon (DOC) reduction. Odencrantz *et al,* (2001) suggested MNA should only be considered where there is confidence in the data, sound understanding of processes and well designed monitoring. Failure to do so may result in seriously underestimated contamination, as reported by Eberhardt and Grathwohl (2002), and consequently severe environmental hazards.

5.2 Initial Conceptual Model of Acid Tar Lagoons

An initial conceptual model of an acid tar lagoon based on information gathered from the literature and site visits is shown in Figure 5-2, which depicts a range of processes and potential migration pathways that have been observed or are inferred for a general acid tar lagoon.

It should be noted that not all items on the conceptual model have been confirmed and may be updated during the research. However, the model provides a useful starting point.

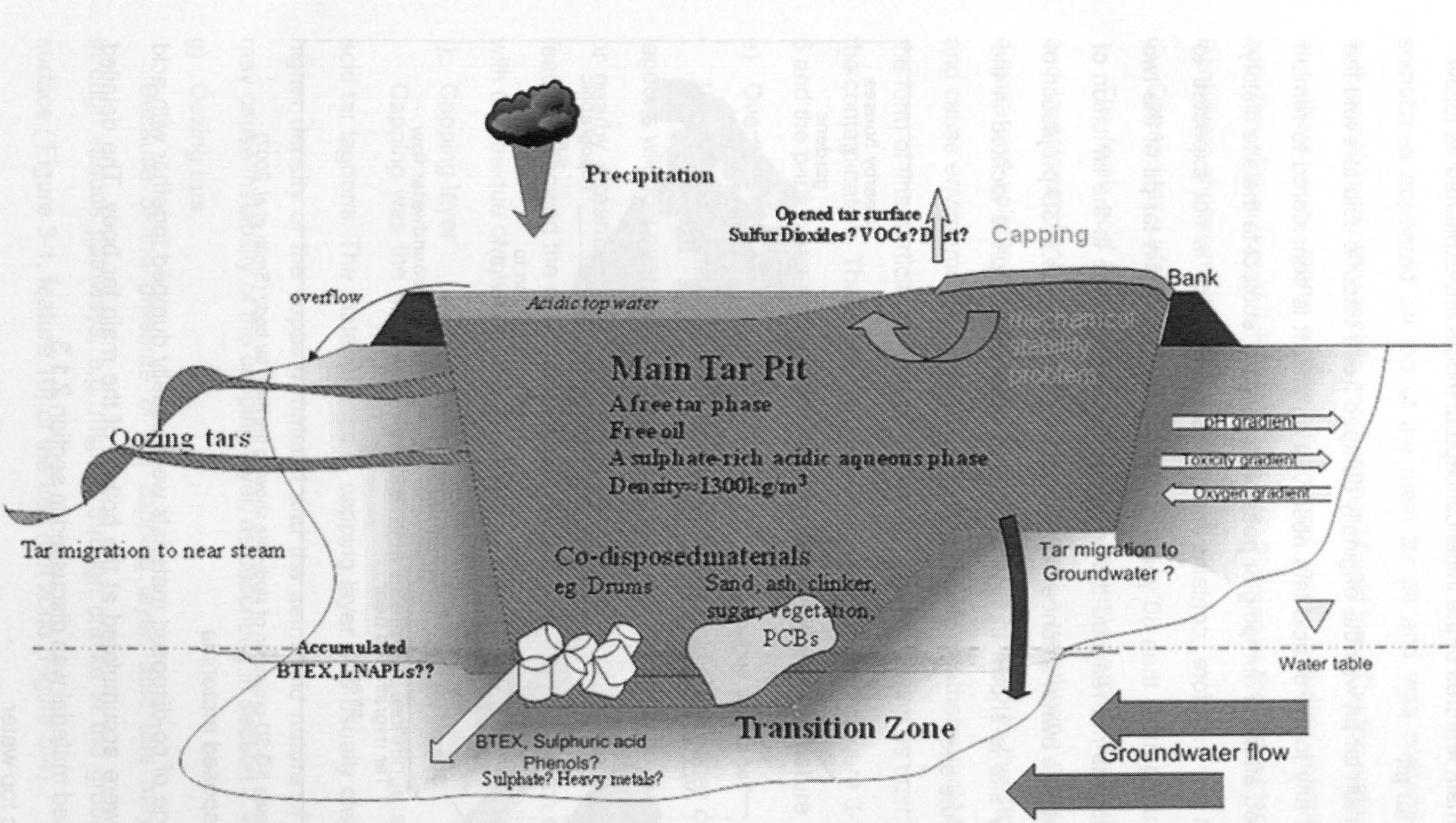


Figure 5-2 Conceptual Model of Acid Tar Lagoon

The main features of the initial conceptual model are explained as follow:

a) Main tar pit

The main tar pit was the originally dumped fresh viscous acid tars and the source of any forms of acid tars observed on site. It is considered to remain undisturbed after the dumping or possible treatment, subject to the site history. The main tar, therefore, contains mainly fresh tar which is not expected to change during more than 30 years of site history. The main tar pit of the two study sites was not reached during this PhD research due to the limitation of equipment, site owner's concern and health & safety issues. A 3D-projection of one study site is shown in Figure 5-3 and the main tar pit is located in the middle of the site.

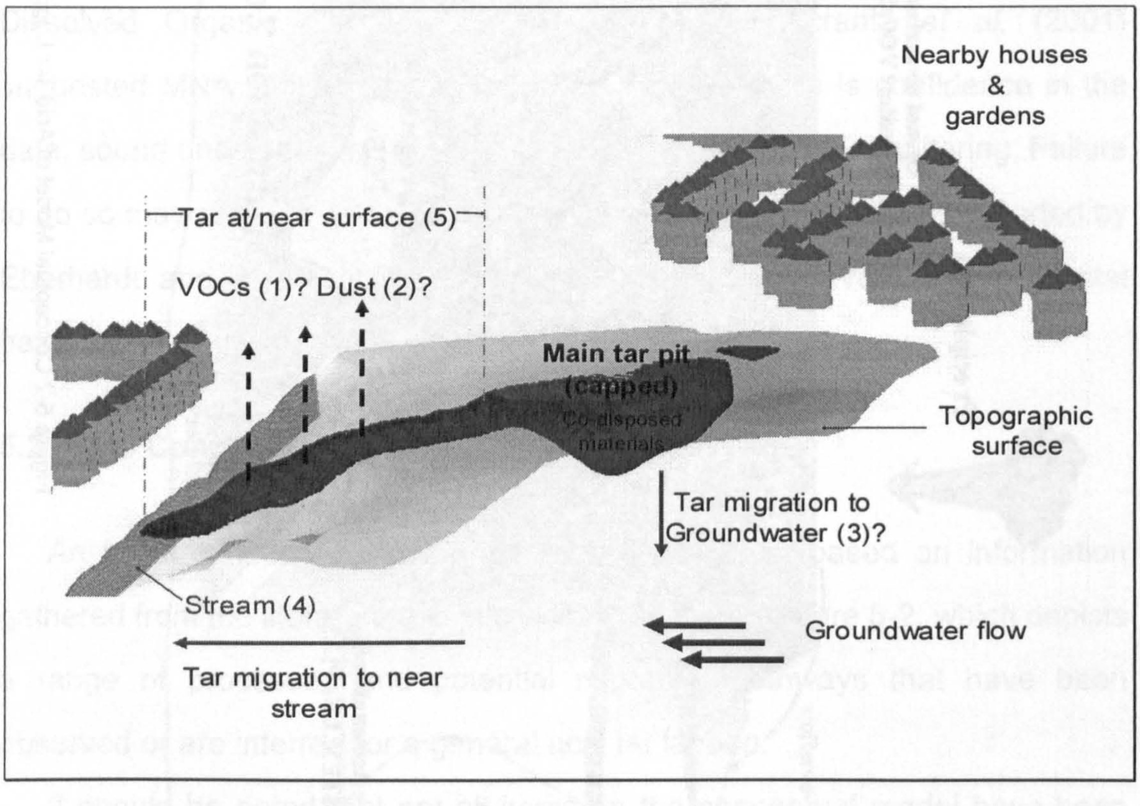


Figure 5-3 3D-projection of study site showing the main tar body (Smith *et al*, 2007)

b) Co-disposed materials

A range of co-disposed materials were usually dumped together with acid tars and were accumulated at the bottom of the main tar body. The detailed co-disposed material was discussed in section 2.1.3.

c) Acidic top water

For uncapped acid tar lagoons, a layer of accumulated rain water sometimes appeared on top of the main tar pit and was contaminated by sulfuric acid and other mobile components of acid tars. The top water is acidic and there were many activities occurred in it, including microbiological activities, dispersion of lighter organics etc. Pictures of the top water of Hoole Bank were shown in Figure 3-1, feature 1-3.

d) Opened tar surface

The fresh acid tars directly exposed to the environment were weathered and transformed into weathered tars. During the weathering process sulfur dioxide and volatile organic compounds may be released to the atmosphere and cause environmental problems. The completely weathered acid tar was in the form of fine particles, which could be blow offsite by wind as dust to spread the contamination. The weathered tar surface was shown in Figure 3-1, feature 5 and the particulate weathered tar was shown in Figure 3-1, feature 7.

e) Overflow

When precipitation exceeds evaporation, the acidic top water of acid tar lagoons will flow over the bunds of the lagoon and contaminate surface water or nearby streams, which may cause additional contamination. Figure 3-1, feature 4 showed the overflow of Hoole Bank acidic top water which contacted with the residue of a wastewater treatment facility.

f) Capping layer

Capping was the most common previous treatment technique applied to acid tar lagoons. The material used in capping layer was usually clay and the higher density of the capping material and the semi-fluid nature of acid tars may cause instability of the capping layer, as described in section 2.4.1.

g) Oozing tars

Because of the pressure of the capping layer, acid tars may migrate through various pathways, e.g. migrate through cracks in the ground to the surface (Figure 3-1, feature 10) or the tree root zone (Figure 5-4).

Figure 5-4 Acid Tar migration through tree root zone.

h) Tar migration to nearby stream

If the tar migration reached any nearby stream, the leaching of hazardous components into surface water will be significantly exacerbated, as shown in Figure 5-5.

i) Transition zone

The transition zone was proposed to describe the interface between acid tar lagoon and surrounding environment. Depending on the properties of the acid tar, the mobile components of acid tars or acid tars themselves may smear certain extent of soil and groundwater surrounding the main tar pit and form a heavily contaminated area around the acid tar lagoons. Many physical, chemical and microbiological processes in the transition zone tend to spread or limit the contamination.

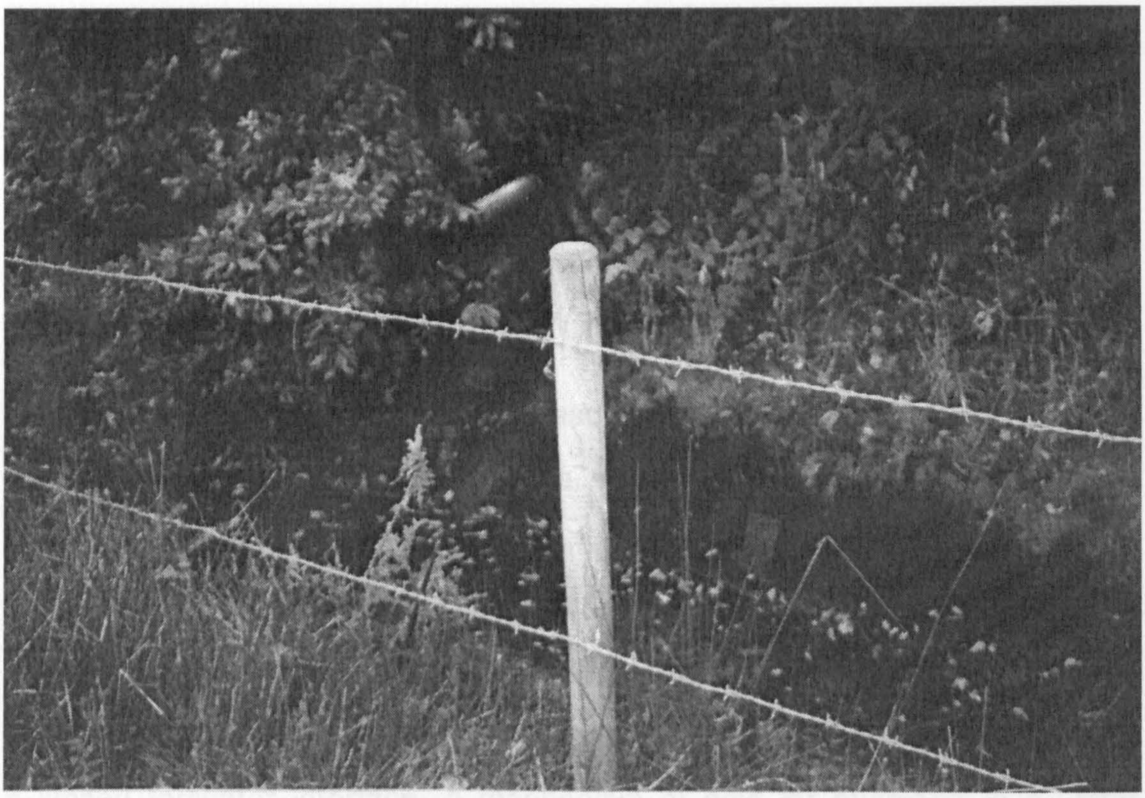


Figure 5-5 Tar migration to nearby stream.

j) pH, toxicity and oxygen gradient

Within the transition zone, the level of contamination decreased with distance from the tar pit, which generated the gradients of pH, toxicity and oxygen gradients. It should be noted that the oxygen gradient is controlled by microbiological activities and depth in the soil. The direction of the gradient may, therefore, vary.

k) Tar migration to groundwater

Acid tar migration may also happen underground and if the fresh tar reached the groundwater, a hhigh level of groundwater contamination may occur.

l) Accumulated BTEX, LNAPLs

The lighter organic components of acid tars, such as BTEX or LNAPLs, may accumulate in the upper section of the groundwater. It should be noted that such a feature is not direct supported by any observational evidence and needs to be validated.

m) BTEX, sulfuric acid, phenols, sulfate and heavy metals (water leachable components

Water soluble components of acid tars may leach during the long history of acid tar lagoons and cause groundwater contamination.

Some of the processes shown in this conceptual model are issues that may be addressed by applying MNA as a management strategy, especially for the surface water and transition zone, as will be further discussed in Chapter 9.

The following three chapters present the results of laboratory work that have been carried out during this PhD project. They are drafted in the form of three research papers, and are presented in the format of a paper published in a journal.

Chapter 6: Weathering and leaching characteristics of acid tars, discusses the leaching behavior of viscous tar and weathered tar samples collected from the two study sites using batch and cascade leaching tests. This chapter also proposes a conceptual model of the weathering process of acid tars by correlating the leaching test data and site visit observations.

Chapter 7: Flow cell leaching test of acid tars, further investigates the leaching behavior of viscous tar in a simulated groundwater in a model soil. This chapter addresses the long term leaching characteristics of acid tars with a limited tar/water interface. A mechanism of acid tar migration in a water saturated porous media is also proposed.

Chapter 8: Physical and chemical analysis of acid tars, discusses the development of analytical techniques applied to acid tars during this PhD project. This chapter also discusses the correlation of data from different analytical methods to build up a more complete picture of acid tar composition and hence its potential environmental impact.

Findings from the three research papers are drawn together in Chapter 9: Discussion, and considered in the context of the thesis of this PhD, that MNA is a potentially viable option for the environmental management of some acid tar lagoons.

Chapter 6 Weathering and Leaching Characteristics of Acid Tars

Hao Xu and Smith Colin

Abstract

Acid tars are an industrial waste product, that when inappropriately disposed of, can pose potential risks to human health and the environment because of their high acidity, hazardous constituents and their unique behaviour, such as weathering and bulk migration. This paper examines the leachability and weathering characteristics of various forms of acid tar samples collected from two acid tar lagoon sites in the North of England, which were produced by oil rerefining and benzole refining processes. Solid to liquid ratio 1:10 agitated batch, and cascade leaching tests with cumulative solid to liquid ratio 1:60 were carried out on all forms of acid tars. The results showed that unweathered acid tars leached high level of acidity, sulfate and Total Organic Carbon, while weathered forms of acid tars leached lower levels of contamination, but over prolonged periods. A model of weathering processes of acid tars is postulated based on field observations and the observed leaching behavior in the laboratory. It is estimated that the timescale required for an unremediated acid tar lagoon to stabilize will be many centuries.

Keywords: Acid Tar, Batch Leaching Test, Cascade Leaching Test, Weathering.

6.1 Introduction

Acid tars are defined as tars of high sulfuric acid content that have arisen as by-products of benzole refining, refining petroleum fractions (particularly white oil) and oil re-refining (Milne et al 1986). Historically these waste products were typically dumped in converted holes in the ground to form lagoons and now form significant bodies of contamination that can result in hazard to human health, controlled waters and the natural environment. In-situ, acid tar comprises a mass of hydrocarbons that is generally viscous with very low pH. The main potential hazardous components of acid tars are Polycyclic Aromatic Hydrocarbons (PAHs), phenolic aromatic hydrocarbons, Benzene, Toluene, Ethylbenzene and Xylene (BTEX) and sulfuric and organic acids (Nancarrow et al 2001). After years of weathering, acid tars may present in a range of different forms on-site, each of which have different physical and chemical characteristics.

The environmental impacts of acid tar lagoons can include bulk tar migration, surface and groundwater contamination and soil contamination (Talbot et al, 2004). One of the major potential contamination pathways is the leaching of water soluble components of acid tar into groundwater flow and surface runoff. The water soluble components of acid tar also play important roles in the weathering process and migration of acid tars. Understanding the leaching characteristics of acid tars is a key factor in assessing the environmental impact of an acid tar lagoon. At present there is a severe lack of data on all aspects of acid tars in the literature with all current work confined to general descriptions of sites, remediation methods or the production process. The aim of this paper is to present new data and interpretations on the following:

i) the nature and characteristics of the leachable components of acid tars;
ii) the modification of tar characteristics by the leaching process;
iii) leaching duration timescales with respect to:
    a) hazardous levels of contaminants,
    b) all leachates.

Since acid tars arise from a range of different processes, it is not possible to address all tar types. Instead this paper focuses on tars sourced from two lagoons as a first stage in elucidating generic characteristics.

6.2 Materials and Methods

6.2.1 Acid tar samples

The acid tar samples for this work were collected from two acid tar lagoons in the north of England which will be termed Site A and Site B. Site A is located at Hoole Bank (Nichol, 2000 and is an open acid tar lagoon which contains approximately 62 000 tonnes of acid tars, produced as a by-product of oil re-refining. The site occupies an area of approximately 3.5 hectares. The main lagoon is contained within an elevated bund and has approximately 0.4 meters of ponded water above the tars. External to the main lagoon, there is a large area of upwelling tar and a number of smaller upwelling areas around the bund of the main lagoon. Site B is a capped site containing approximately 60 000 tonnes of acid tars from the benzole refining industry. At this site, acid tars are migrating out of the ground through fissures in the capping layer and moving down gradient on the surface.

At both sites, samples were collected at shallow depth at locations across the site, and were observed in a range of physical forms as described in Table 6-1:

Site	Name	Description
A	Viscous Tar	viscous acid tar samples (assumed to be fresh, unweathered tar) obtained from a location of large scale upwelling tar (AU1) adjacent to the main lagoon (sample depth: 0.3-0.5 meters)
A	Odourous Viscous Tar	viscous acid tar with significant acidic smell (assumed to be fresh, unweathered tar) obtained from a location of large scale upwelling tar (AU2) adjacent to the location AU1 and under tree cover (sample depth:

		0.0-0.1m)
A	Semi-solid Tar	Semi-solid tar sampled from a tar upwelling location adjacent to the main lagoon (AU3). The tar was sampled below the weathered surface layer. (sample depth: 0.2-0.3 meters)
A, B	Weathered Friable Tar	black, powdery, dry weathered tar from a dry, crusted over upwelling location (sampled on the surface) in both Site A (AU4) and Site B (BU1)
A	Weathered Green Tar	green coloured, tough clay like weathered tar, containing some soil, obtained from the hard crust of the main lagoon under the ponded water (AS1). (sample depth: 0.2-0.3 meters below tar surface, under top water)
A	Weathered Black Tar 1	black, clay like weathered tar obtained from a dry, crusted over area at location AU3 (sampled on the surface)
A	Weathered Black Tar 2	black, clay like weathered tar obtained from an upwelling location (AU5) adjacent to AU3, sampled on the surface.
B	Weathered Black Tar	black, clay like weathered tar obtained from surface of Site B
A	Weathered crystalline tar	dry, hard weathered tar with dark green and black color, obtained at the edge of an upwelling location under tree cover (AU6) close to AU4, sample depth: 0.1-0.2 meters, under Weathered Friable tar)
A	Lagoon Top Water	acidic water samples from the water ponding above the main lagoon.

A	Soil	soil samples obtained from the centre of a small vegetated 'peninsula' protruding onto the main lagoon, excavated just below the level of the ponded water.

Table 6-1 acid tar samples

Note: Label AU1-6 refer to sampling locations around Site A. AU1 and AU2 were located south of the lagoon at a location of major acid tar upwelling. AU6 was located at the south edge of the major upwelling. AU3, AU4 and AU5 were located around northwest side of the lagoon. It should also be noted that Weathered Black Tar 1 and Semi-solid Tar were both sampled at location AU3, where the weathered black tar 1 was sampled on the surface and the semi-solid tar was sampled by excavation.

It is recognized that the physical descriptions given above are of necessity very qualitative and in some cases, e.g. liquid/semi-solid, somewhat subjective. The development of quantitative index tests should be a goal of future work.

There is an additional question of whether the weathered tars are genuinely weathered from the original acid tar or are a result of mixing with stabilizing materials. The assumption made in this paper is the former as such tars are found at locations of fresh upwelling tar and are assumed to be the weathered products of such which were clearly not recently treated. The one exception is the Weathered Green Tar, which appeared to have some soil mixed in with it.

6.2.2 Leaching procedure

6.2.2.1 Batch Leaching Test

The batch leaching test procedure selected was a modification of the British Standard: BSEN12457-2:2002 Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction). The main modification to the British Standard test concerns size reduction prior to the agitation which is unachievable for acid tar samples because of their viscous nature. The specific procedure employed was as follows:

1. Place (10 ± 1) grams of acid tar in a flask.
2. Add sufficient purified water to establish a liquid to solid ratio (L/S) = 10 L/kg ± 2% and seal the flask. Care should be taken to obtain good mixing of solid and liquid.
3. Agitate for (18 ± 0.5) hours.
4. Allow the suspended solids to settle for (60 ± 5) minutes after agitation.
5. Filter the leachate using a vacuum filtration using a 0.45 μm filter.
6. Measure immediately pH, conductivity, temperature and turbidity of the leachate.
7. Retain leachate sample for chemical analysis

6.2.2.2 Cascade Leaching Test

While the one stage batch test is a good initial indicator of leaching behaviour, multistage cascade tests give a clearer picture of the long term leaching characteristics (Czerewko et al., 2001).

The cascade leaching test employed comprises a sequence of batch leaching tests that achieve a higher accumulative liquid to solid ratio. The first stage of the procedure follows the batch leaching test as described in 2.2.1 (except a 1:2 S/L ratio is used). Stage 8 then comprises return of the leaching residue retained on the filter together with the filter paper back to the flask and mixing with additional purified water to achieve a specified cumulative liquid to solid ratio. The flask is sealed and Stages 3-7 of the batch leaching test are then repeated. This process is repeated for all required cumulative liquid to solid ratios. The cumulative liquid to solid ratios used in this work were: 1:2, 1:10, 1:20, 1:30, 1:40, 1:50, and 1: 60. Thus in Stage 1 a S:L=1:2 ratio was used. In stage 2 this was increased to 8:1 ratio. All remaining stages employed a 10:1 ratio. Since the acid tar is physically sensitive to agitation and breaks up easily, two sets of cascade tests were carried out, one with low rate agitation and one with no agitation. The former ensures results are not limited by diffusion kinetics; the latter better simulates field conditions.

6.2.3 Analytical methods

6.2.3.1 Inorganic components

The pH was measured by a pH meter and inorganic components in the leachate were measured by DIONEX DX-120 Ion Chromatography (Column type: IonPac CG12A cation exchange column and IonPac AS14A anion exchange column). Analytes measured were: chloride, sulfate, sodium, ammonium, potassium, magnesium and calcium. Of these, only sulfate was present in significant levels. All the other inorganic components were less than 150mg/L. As a result only pH and sulfate levels will be reported in the results.

6.2.3.2 Organic components

Detailed analysis of the organic components of acid tar leachate is a complex topic and beyond the scope of this paper. Instead Total Organic Carbon (TOC) will be used as an indicator for the organic components of the leachate. TOC was measured using a SHIMADZU TOC-V CSH TOC Analyzer.

The anticipated organic components (Nancarrow *et al*, 2001) in the leachate are listed in Table 6-2.

Organic Components	Solubility
Benzene, Toluene, Ethylbenzene & Xylene (BTEX)	moderate
Phenol	moderate
Polycyclic Aromatic Hydrocarbons (PAHs)	low
Organic Acids	soluble
Sulfur containing organics [1]	moderate
Other Aliphatic organics [2]	insoluble
Other Aromatic organics [2]	insoluble

Table 6-2 Anticipated organic components

Note: 1.The table lists anticipated organic components by groups, which may overlap with each other.

2. The sum of the Aliphatic and Aromatic hydrocarbons is termed Total Petroleum Hydrocarbons (TPH), which covers the C5-C35 range of organic components.

Initial more detailed organic chemical analysis, including Head Space extraction followed by Gas Chromatography - Flame Ionization Detector (GC-FID), Solid Phase Micro Extraction (SPME) followed by Gas Chromatography – Mass Spectrometry (GC-MS) and High Performance Liquid Chromatography (HPLC), show no BTEX, phenol or PAHs in the leachate of Site A and only trace concentration of Other Aromatics.

Relatively high levels (>100mg/L) of TOC were observed in some samples, which is unlikely to be entirely due to the soluble organic components. While difficult to measure, it is expected that the soluble organic components consists mainly of organic acids. The remaining quantity is ascribed to colloids, suspended in the aqueous phase, but small enough to pass through the 0.45 μm filter (Bergendahl and Grasso 1998).

Such colloids are organic or inorganic particles with a diameter from 1nm to 0.45 μm and have to be considered in leaching tests when strongly sorbing (i.e. likely to clump together as colloids) organic compounds (e.g. PAHs) are concerned (Hansen, 2004). The presence of colloids usually results in a large apparent fraction of soluble organic compounds being indicated in the aqueous phase than actually exist. In this paper, the effect of colloids is considered as a contribution of organic contamination to the leachate.

6.3 Results

6.3.1 Batch leaching tests

The results of the batch leaching tests are shown in Figure 6-1. This indicates that the Odorous Viscous Tar yields extremely high sulfate levels and also has a correspondingly low pH. The other tar samples (with the exception of Weathered Black Tar 2) all generate a similar low pH and broadly similar sulfate levels. This is particularly surprising for the weathered tars, for which it was assumed that most of the contaminants would already have been leached away. The Viscous and Semi-solid acid tar samples have significantly higher TOC values than the weathered tar samples. The soil sample which was collected from a peninsula protruding into the lagoon has low acidity, zero TOC and relatively high level of sulfate. Such a feature is mainly because the soil is saturated with the lagoon top water, which has high sulfate level. The acidity may be neutralized by the soil and vegetation. At this site, it was observed that the soil and vegetation around the lagoon edge was coated in a thin layer of black material assumed to be the colloidal tar, this the organic colloids are likely to have been adsorbed by the soil at the edge of the sampled peninsula which was preventing further contamination of the soil at the peninsula centre.

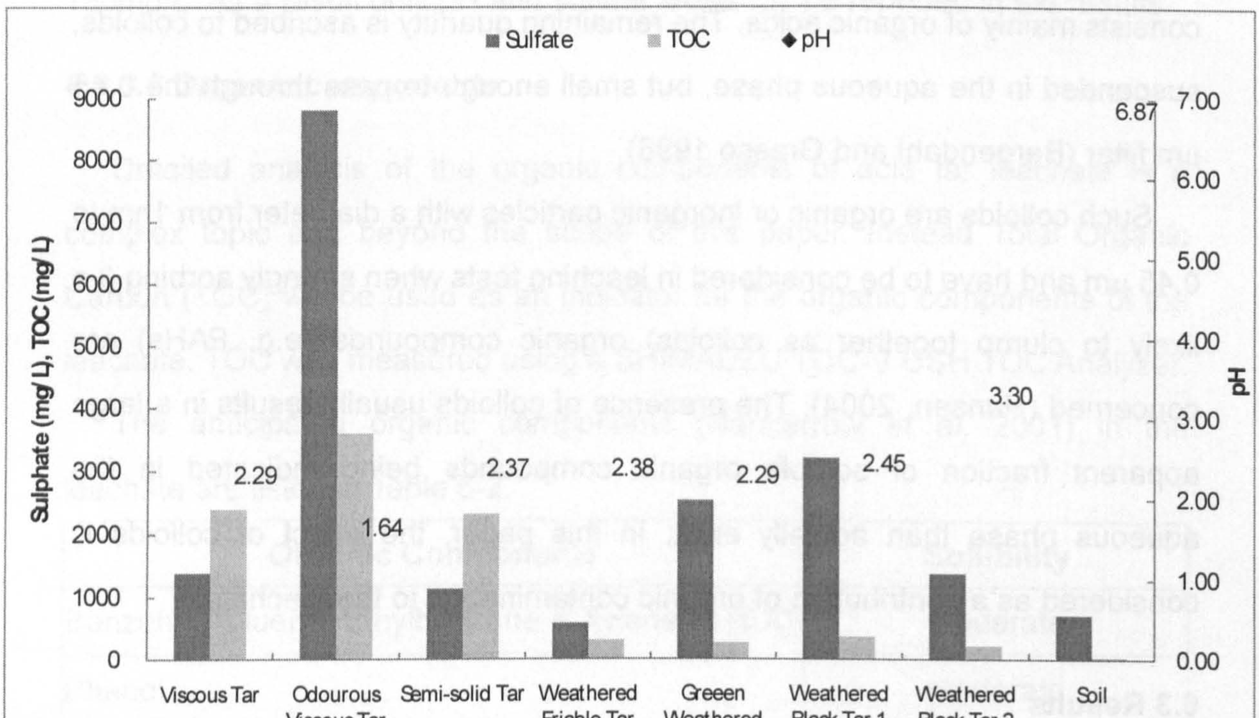


Figure 6-1 Batch leaching test results

The batch leaching test results are indicative of the worst case scenario of leachability by exposing the acid tar samples to relatively long mixing time at a high rate of agitation. During the batch tests all the acid tar samples broke down into small particles to form a suspension except weathered black tar and weathered crystalline tar. 10 minute centrifuging of such a suspension at

8000rpm was only able to settle out part of the suspended solids. The results show that under these conditions, most acid tar samples are capable of generating high levels of contaminants. However the physical breakdown of the tars into colloids may result in misleadingly high soluble leaching rates.

6.3.2 Cascade leaching tests

6.3.2.1 Influence of Agitation

Two sets of cascade tests were performed, under non-agitated or slow agitated (roller table 10 rpm) conditions. Figures 6-2 (a) and (b) compare the results from the two sets of tests on the viscous tar and indicate broadly similar results with no strong trend distinguishing each set of tests. Since this pattern was observed for all samples, the results presented in the remaining sections are all taken from the slow agitated cascade tests. However, it may be noted that there are moderately large difference in some of the results. This can also be seen when comparing the batch test data with the 1:10 stage cascade data.

The variation of test data is attributed mainly to the heterogeneous nature of acid tars. Although being sampled at same location, each sample of acid tar is not necessarily homogeneous with other samples, especially viscous acid tars. Repeat tests were carried out for all batch samples and randomly selected tar types in the cascade tests, which were sampled twice from same sample bottle and then subjected to the same test procedures. The data of both batch test and repeat cascade tests showed adequate repeatability with less than 5% error. More detailed discussion concerning the repeatability of IC analysis is given in Chapter 8.

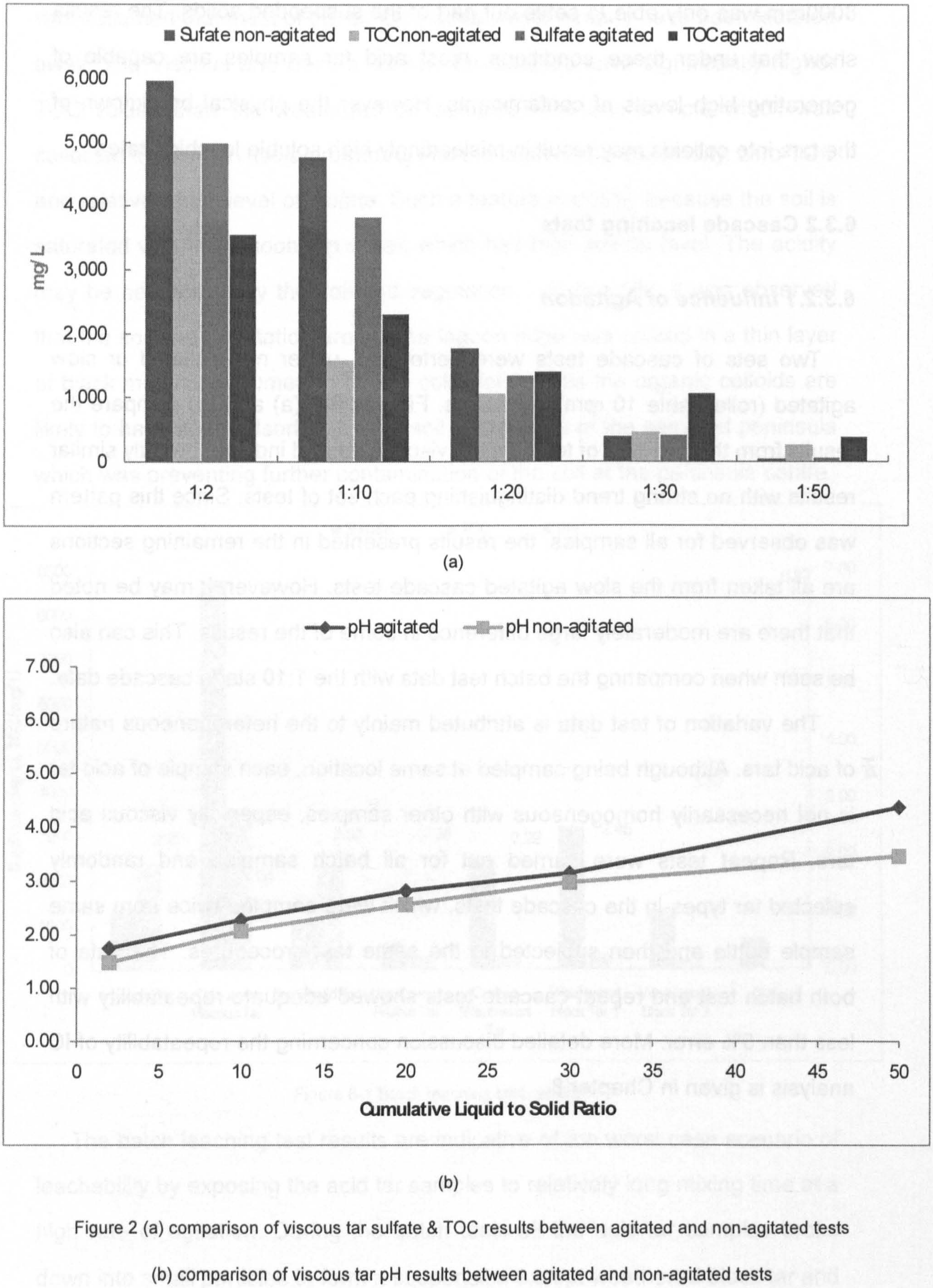


Figure 2 (a) comparison of viscous tar sulfate & TOC results between agitated and non-agitated tests

(b) comparison of viscous tar pH results between agitated and non-agitated tests

6.3.2.2 Leaching of pH, Sulfate and TOC.

Figures 6-3 – 6-8 present pH, sulfate and TOC results for each of the various tars sampled.

Figure 3 presents data for viscous tar. It yields the highest initial sulfate and TOC levels and also the lowest pH. The sulfate and TOC declined quickly in the later stages, while the pH increased gradually. To best simulate field leaching conditions, it was decided not premix and attempt to homogenize the sample due to risk of physical degradation and chemical breakdown (e.g. release of SO_2). The 1:10 results differ by approximately a factor of 2 from the batch test data due to the previously mentioned heterogeneous nature of acid tars. The distribution of acids and lighter organics are not homogeneous, even in the same original sample, which was approximately 1kg in mass.

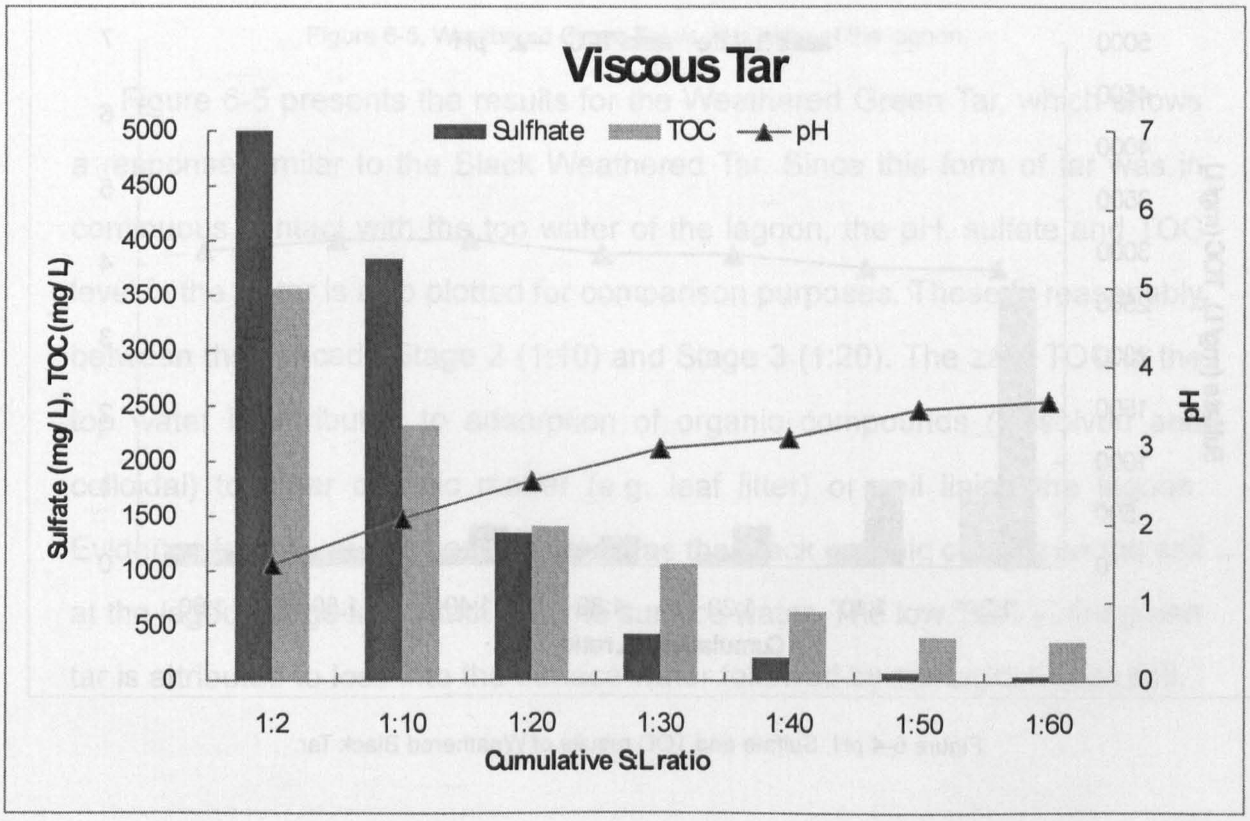


Figure 6-3 pH, Sulfate and TOC results of Viscous Tar

The leaching characteristics of the fresh viscous acid tar samples may be regarded as an upper bound to the field leaching rate of acid tars. When acid tar is freshly deposited in an un-engineered site, there will be an initial flush of leachates released to the surface water system (and to the groundwater system if the lagoon is located in permeable strata). As the outer fresh tar loses its water soluble components, it may weather into alternative, more stable forms. Weathering pathways will be examined in more detail in Section 6.4.1.2.

Figure 6-4 shows the results for Weathered Black Tar. It has around half of initial level of sulfate of fresh viscous tar and a significantly lower TOC, which all declined quickly at later stages. The pH level is relatively stable around 4, indicating strong buffering like behaviour but always higher than the fresh viscous tar. It usually appears in the middle of tar migration pathways, indicating an intermediate form of the weathering processes.

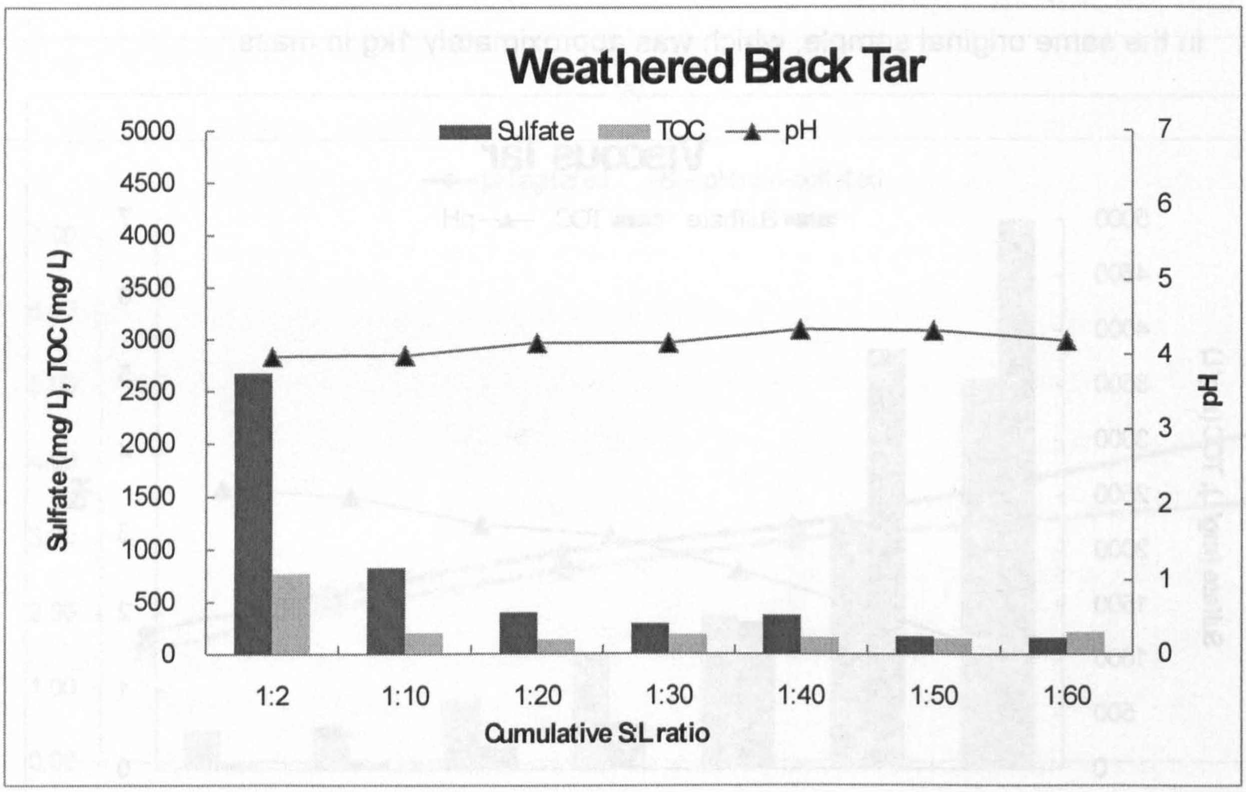


Figure 6-4 pH, Sulfate and TOC results of Weathered Black Tar.

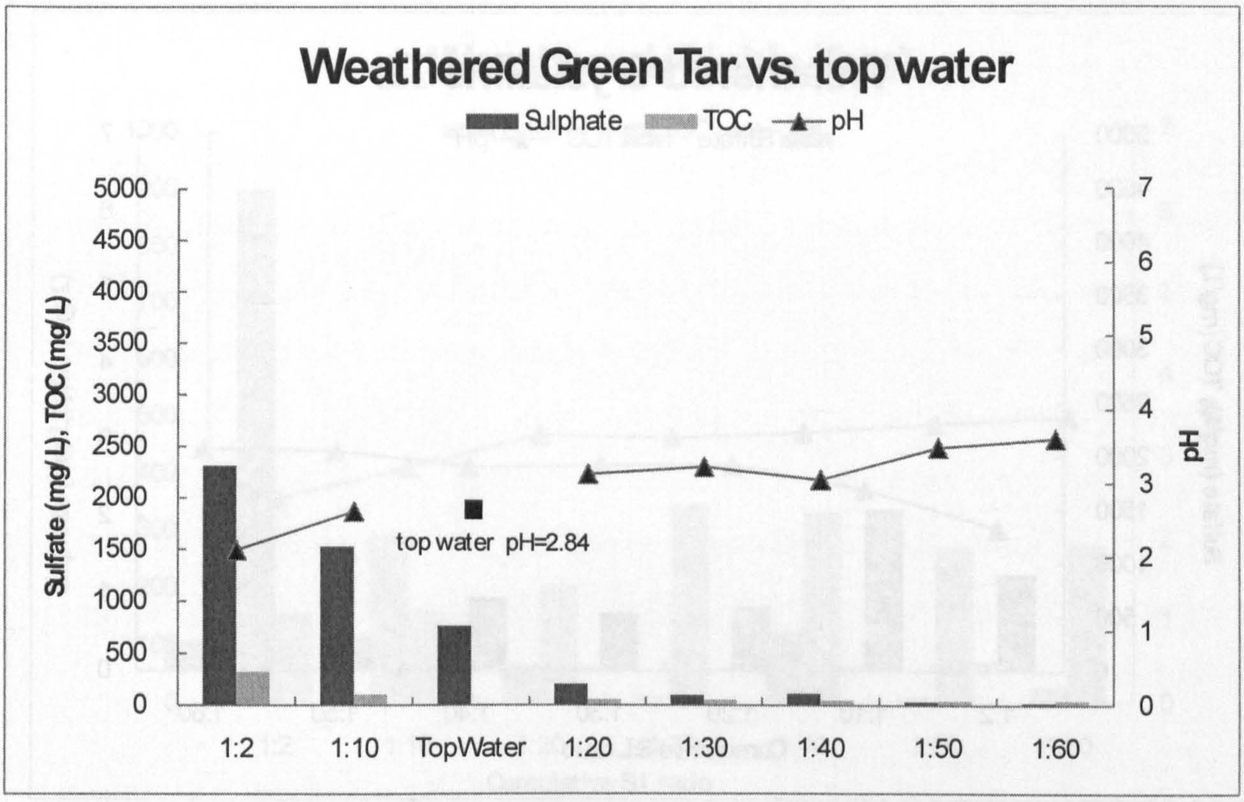


Figure 6-5, Weathered Green Tar vs. top water of the lagoon.

Figure 6-5 presents the results for the Weathered Green Tar, which shows a response similar to the Black Weathered Tar. Since this form of tar was in continuous contact with the top water of the lagoon, the pH, sulfate and TOC level in the water is also plotted for comparison purposes. These fit reasonably between the cascade Stage 2 (1:10) and Stage 3 (1:20). The zero TOC in the top water is attributed to adsorption of organic compounds (dissolved and colloidal) to other organic matter (e.g. leaf litter) or soil lining the lagoon. Evidence for this, as previously noted was the black organic coating on the soil at the lagoon edge in contact with the surface water. The low TOC in the green tar is attributed to loss into the surface water followed by adsorption onto soil.

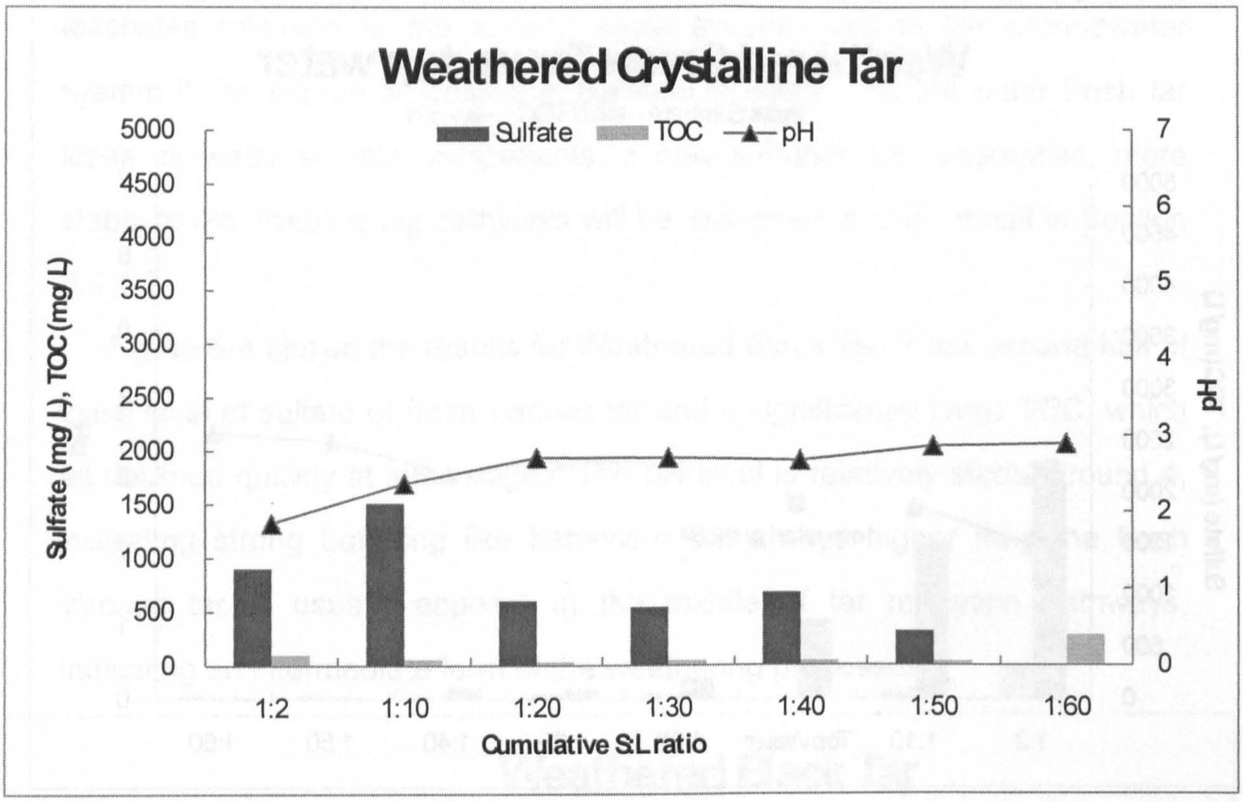


Figure 6-6 pH, Sulfate and TOC results of Weathered Crystalline Tar

Figure 6-6 shows the results for Weathered Crystalline Tar. It has lower sulfate and TOC level than Weathered Black Tar but higher acidity. Its pH is even lower than viscous tar after stage 4 (S: L ratio 1:30) and the pH of the final stage is below 3. It, too appears to have a strong buffering behaviour. The Weathered Crystalline Tar is dry and hard form of acid tar, which on Site A was found away from the main lagoon, at the edge an tar upwelling location and under the coverage of trees. The reason for the high TOC level recorded at an S:L level of 1:60 is unknown. This anomaly could be caused by measurement errors or possibly be the result of sudden sample breakdown, which would increase its contact area with water.

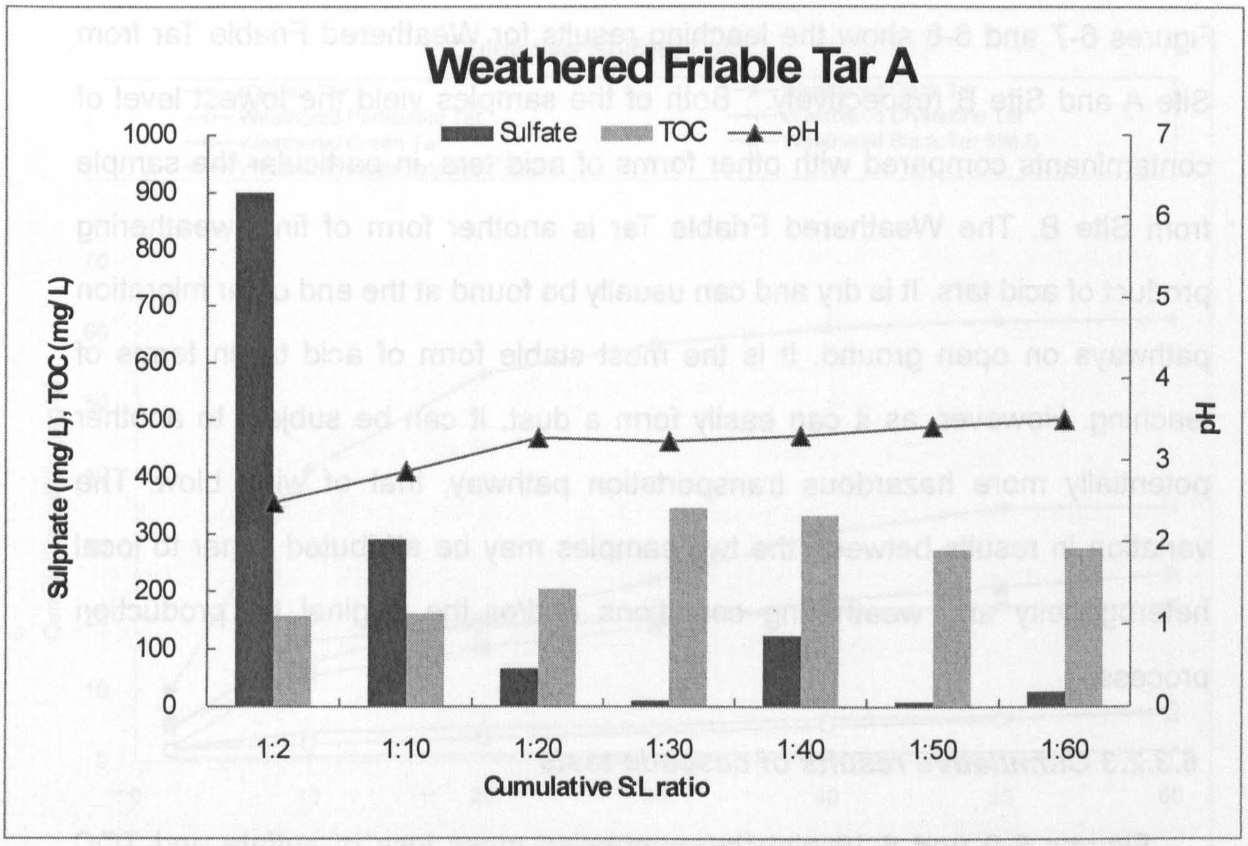


Figure 6-7 pH, Sulfate and TOC results of Weathered Friable Tar of Site A

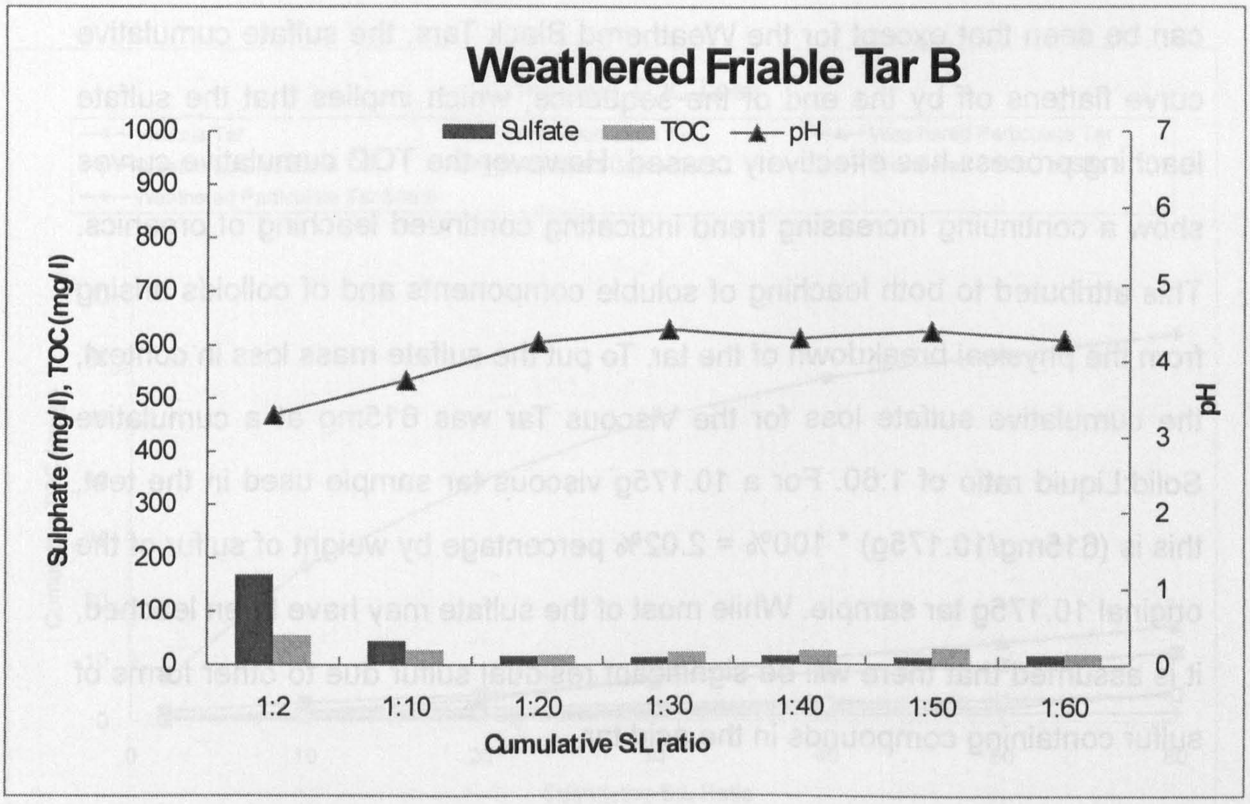


Figure 6-8 pH, Sulfate and TOC results of Weathered Friable Tar Site B

Figures 6-7 and 6-8 show the leaching results for Weathered Friable Tar from Site A and Site B respectively. Both of the samples yield the lowest level of contaminants compared with other forms of acid tars, in particular the sample from Site B. The Weathered Friable Tar is another form of final weathering product of acid tars. It is dry and can usually be found at the end of tar migration pathways on open ground. It is the most stable form of acid tar in terms of leaching. However, as it can easily form a dust, it can be subject to another potentially more hazardous transportation pathway, that of wind blow. The variation in results between the two samples may be attributed either to local heterogeneity and weathering conditions and/or the original tar production process.

6.3.2.3 Cumulative results of cascade tests

Figures 6-9 and 6-10 plot the cumulative mass loss of sulfate and TOC during the cascade tests in the same format as an equivalent column test. It can be seen that except for the Weathered Black Tars, the sulfate cumulative curve flattens off by the end of the sequence, which implies that the sulfate leaching process has effectively ceased. However the TOC cumulative curves show a continuing increasing trend indicating continued leaching of organics. This attributed to both leaching of soluble components and of colloids arising from the physical breakdown of the tar. To put the sulfate mass loss in context, the cumulative sulfate loss for the Viscous Tar was 615mg at a cumulative Solid:Liquid ratio of 1:60. For a 10.175g viscous tar sample used in the test, this is (615mg/10.175g) * 100% = 2.02% percentage by weight of sulfur of the original 10.175g tar sample. While most of the sulfate may have been leached, it is assumed that there will be significant residual sulfur due to other forms of sulfur containing compounds in the acid tar.

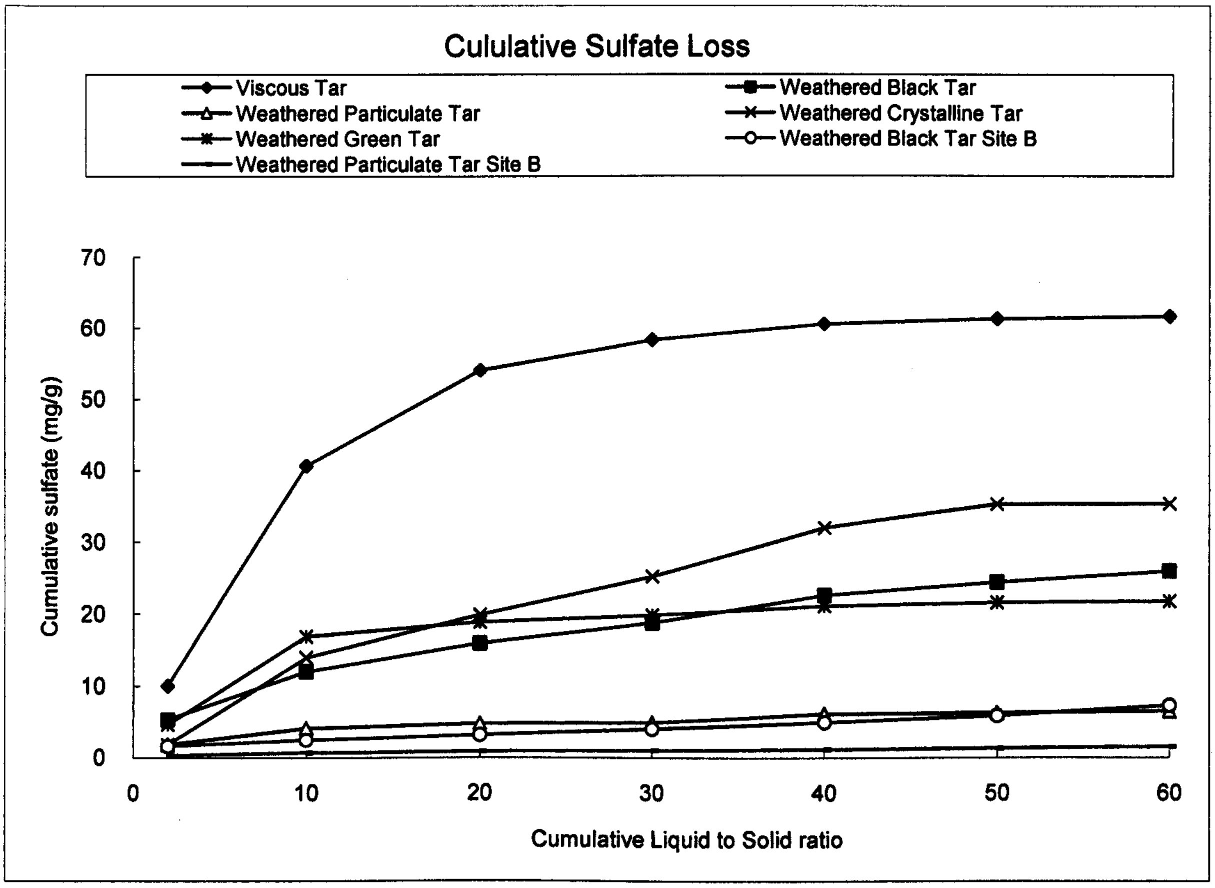


Figure 6-9 Cumulative sulfate lost

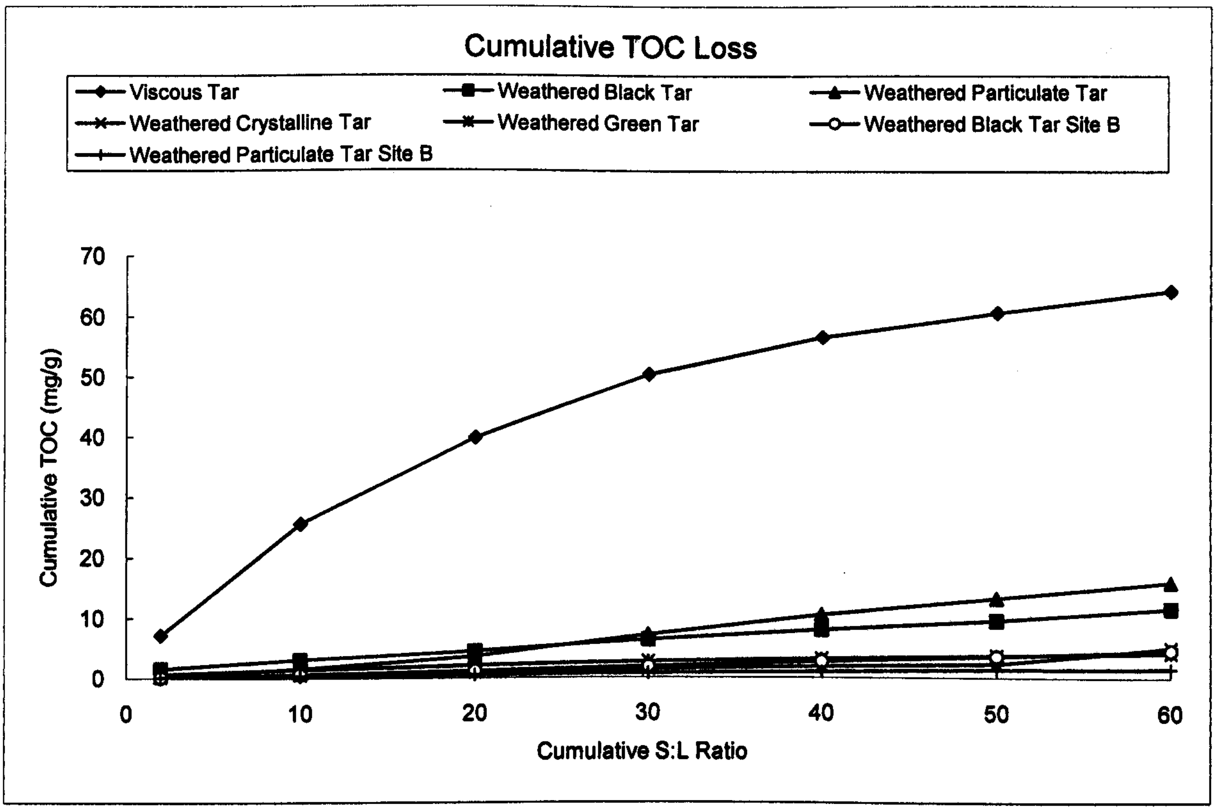


Figure6- 10 Cumulative TOC lost

6.4 Parameter correlation and titration data

6.4.1 Titration

Previous results indicated a strong buffering like behavior in acid tars. A titration test was therefore carried out on a viscous tar sample (mass 8.72g), mixed with water at a 1:10 ratio. The results presented in Figure 6-11 show that the pH of the leachate started at 1.60, equivalent to 0.0021 mol of acidity if assumed to be a pure sulfuric acid non-buffering environment. However the actual system is a buffering system which cost 0.0145 mol of base to lift the pH above 7. This is good evidence of other, presumably, organic acids in acid tar and also explains the relationship between acidity and sulfate. Similar buffering like effects were observed in all acid tar samples during the cascade leaching tests. Such buffering like behavior may also be due to solid/liquid equilibrium processes in the leachate/tar residue system, especially of weathered forms of acid tars. Weathered forms of acid tars usually cannot be completely broken down by slow agitation; equilibrium is therefore established at the surface of the tar residue. Further release of acid into the leachate is controlled by diffusion. It is postulated that this is the reason why most of the weathered tar samples had steady pH during the cascade tests.

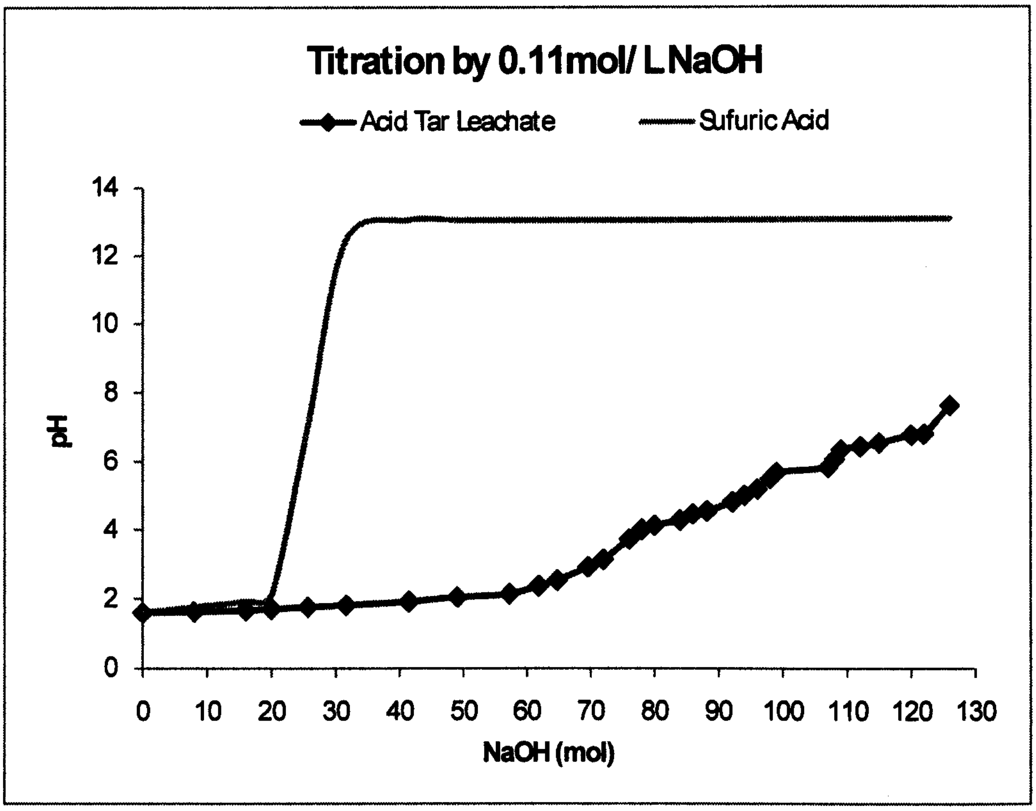


Figure 6-11 Titration of S:L 1:10 Fresh Tar leachate. Dashed line is theoretical titration curve for pure sulfuric acid and sodium hydroxide.

6.4.2 Relationship between acidity, sulfate and conductivity

Electrical Conductivity is a measurement of a material's ability to conduct an electric current. In a solution, it is a parameter that reflects the ion strength of the liquid.

Figure 6-12 plots pH against conductivity from all the cascade test results. It shows a good linear relationship between the two parameters. The plot of log sulfate concentration against conductivity in Figure 6-13 also indicates a good linear relationship for most samples apart from the Weathered Black Tars. The Weathered Black Tar has lower conductivity than the other samples at same sulfate level. This is consistent with Figure 11 which indicated that the Weathered Black Tar had a much lower acidity at any given sulfate level than all other samples.

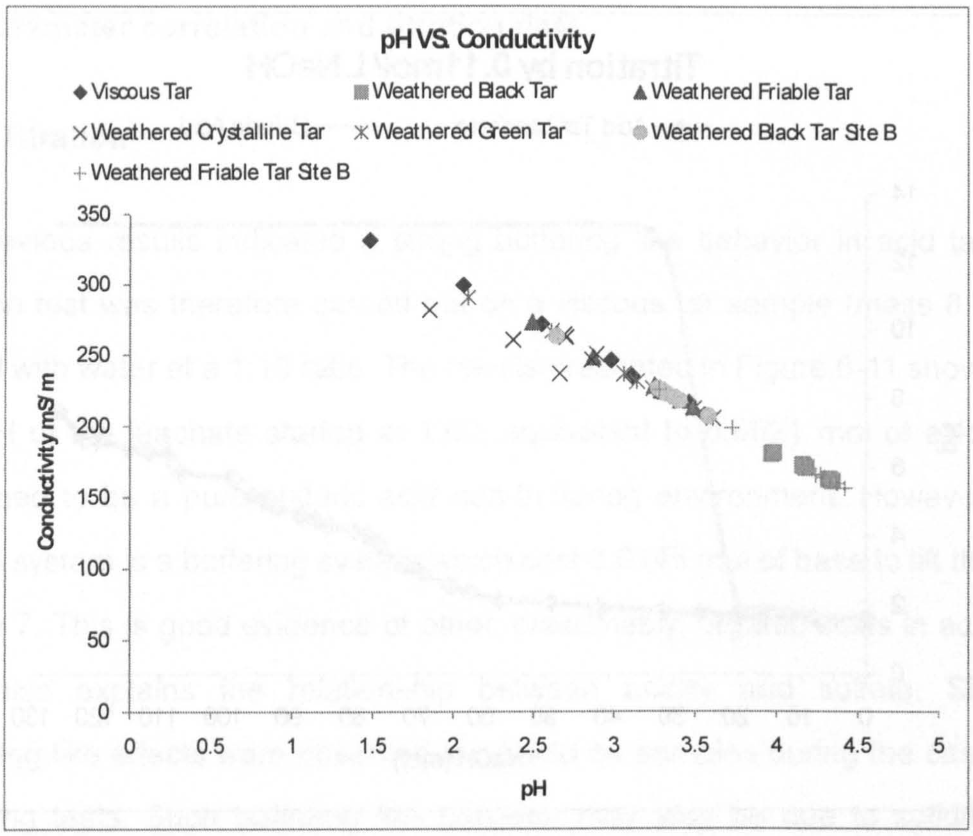


Figure 6-12 Conductiviy & pH.

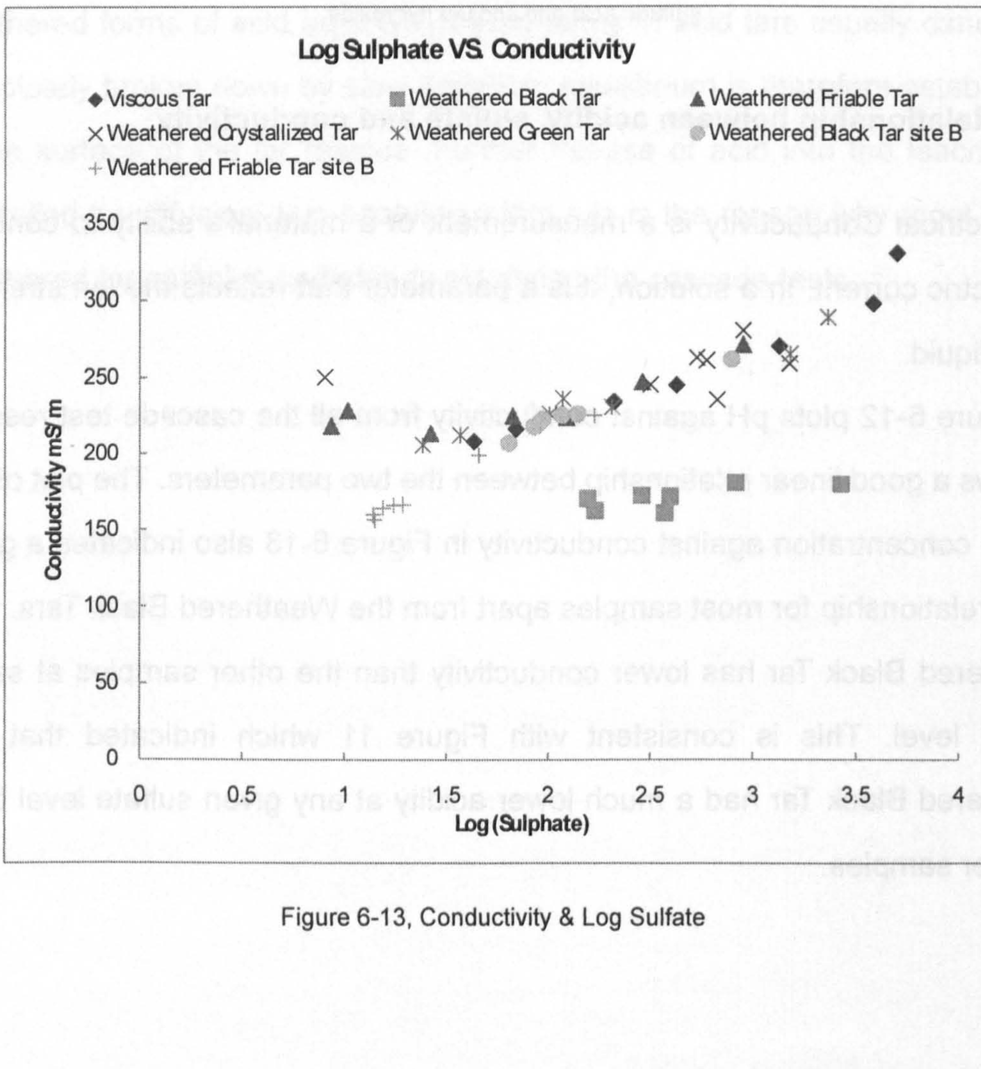


Figure 6-13, Conductivity & Log Sulfate

6.4.3 Relationship between turbidity and TOC

Since many of the tar samples tended to break down into colloidal particles, turbidity measurements were undertaken. Turbidity is a measure of the degree to which the water loses it's transparency due to the presence of suspended particles. As stated in Section 6.2.3.2, colloids are implied as one of the major sources of TOC. Turbidity measurements were taken on all samples of filtered leachates and are plotted in Figure 6-14 against TOC. There is a broad correlation between the two parameters. However the lack of a strong correlation is attributed in part to the fact that tar colloids are not the only source of TOC but also dissolved organics. Data for Viscous tar turbidity was unavailable since it was always out of detection limit, which is an evidence of very high level of suspended particles in the leachate. By eye, it could be seen to form high levels of colloids, and it also generates the highest TOC of all samples.

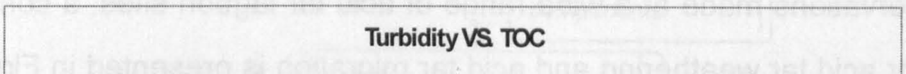


Figure 6-14 TOC & Turbidity

6.5 Discussion

6.5.1 Leaching and weathering

6.5.1.1 Characteristics of acid tar leachates

The batch and cascade leaching tests indicated that the acid tar leachates include not only water soluble sulfuric acid, but other acids which were inferred to be organic acids (sulfonic and carboxylic). The leachate also contains dissolved organic compounds and insoluble organics in the form of colloids. Dissolved inorganic compounds are dominated by sulfate. Weathered tars leach reduced but still significant quantities of leachates compared to unweathered tars.

6.5.1.2 Conceptual model of acid tar weathering

Based on the leaching test data, knowledge gained from previous research, and observations made at a wide range of acid tar lagoon sites, a conceptual model for acid tar weathering and acid tar migration is presented in Figure 16. It must be emphasized that this is a tentative model that requires further validation, but it provides an initial framework for interpreting the conditions observed at acid tar lagoon sites. It may also be subject to modifications to the tar samples due to unknown co-disposed materials, but this is thought unlikely.

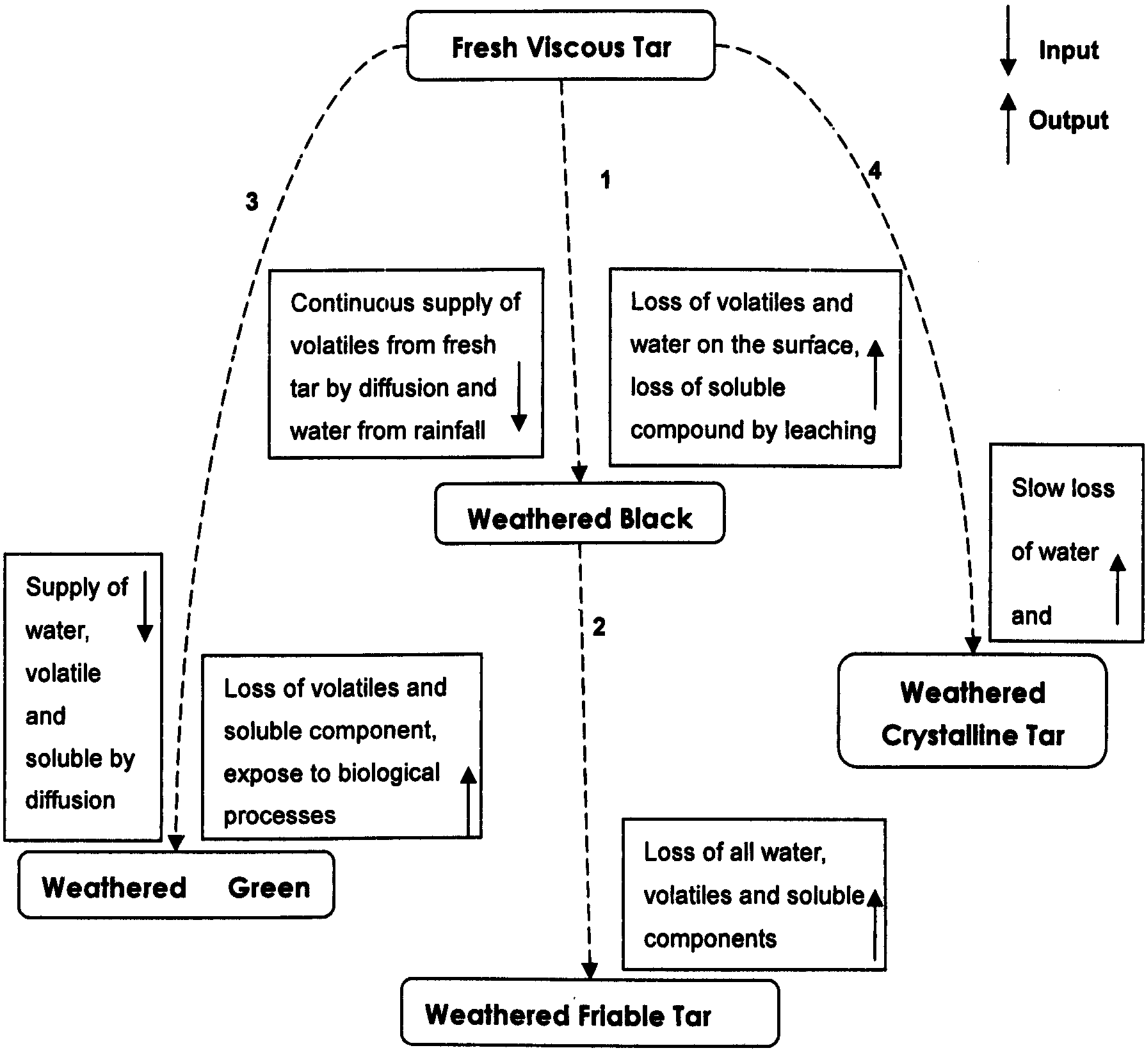


Figure 16 Conceptual model of acid tar weathering processes

Description of weathering processes:

1. *Intermediate weathering process along migration pathways, loss of VOC, and some moisture. Acid leached and reacts with soil*
2. *Final weathering process at the end of migration pathways, loss of VOC and most of the water content presented*
3. *Weathering under lagoon top water, loss of TOC water soluble components, exposure to biological processes.*
4. *Slow furthur loss of moisture, which encourages crystal growth, higher acidity than other final weathered forms.*

The central route of acid tar weathering in Figure 16 (Fresh Viscous Tar - Weathered Black Tar - Weathered Friable Tar) correlates with observations of surface tar migration pathways at many sites. The fresh viscous acid tar primarily loses water (and volatile organic compounds if present) which acts as a solvent during the migration and is transformed into Weathered Black Tar. During this process it is exposed to water leaching from rainfall or water in the ground and loses sulfate and other leachates, but retains a level of moisture content (Thermal Gravimetric Analysis of Viscous Tar, Weathered Black Tar and Weathered Friable Tar showed moisture content of 43%, 10%, and 4% respectively. Following further weathering, leaching of much of the remaining sulfate allowing further loss of moisture, the tar transforms into Weathered Friable Tar and the bulk migration stops (but may continue as dust wind blow). This route had also been observed in lab weathering trials. Viscous acid tar exposed o the air rapidly loses water content and VOCs and transforms into weathered black tar and eventually Weathered Friable Tar. However, weathered black tar in lab trials is much more fragile and less flexible than natural weathered black tar, which is probably due to the accelerated weathering process. In the field, weathered black tar has typically passed through a relatively small fissure in the soil and/or spread out over a relatively large area in a thin layer. It is conjectured that the sulfuric acid reacts with minerals in the soil forming mineral sulphates that reduces acidity but maintains sulfate levels as indicated in Fig. 11. This is likely to alter the physical properties and reduce its fluidity.

The laboratory weathering processes can be reversed. When a lab weathered black tar is placed in the same sealed air space as a sample of fresh viscous tar and can absorb water and volatile organics if present from the fresh tars, the weathered tar becomes mobile again and can migrate further.

It is postulated that if the migration pathway is covered by vegetation or at places where the sun and precipitation is partially blocked, such that leaching is slowed. Then the end weathering product may be Weathered Crystalline Tar which is a much harder and more robust form than Weathered Friable Tar. This is physically quite stable. It is inferred that this form of acid tar is weathered without continuous contacted with water (only losing its water content and volatile organic compounds) thus enabling it to retain its acidity.

Weathered Green Tar appears to form under the top water of open acid tar lagoons, where loss of TOC occurs, but moisture contents and sulfuric acid content are maintained at a high level. It is also possible that microbiological activity is involved in the formation of this tar type.

6.5.2 Practical Implications

In this section the practical implications derived from the experimental data are considered in the context of Site A. This may be generalized with caution to other sites, taking on board the caveat that tars will differ due to their production process. In particular tars arising from benzole refining will tend to contain a higher fraction of lighter organics, and tars arising from white oil production will tend to have a significantly higher sulfuric acid content.

6.5.2.1 Estimate of weathering depth and leaching timescales

It is assumed that at Site A the freshly dumped tar with have rapidly accumulated a pond of surface water and that this will have weathered the tar to a certain depth. Based on the fresh viscous tar cascade leaching results in Figure 3, and the current top water pH of 2.84, this implies leaching to a cumulative level of about 1:30 solid:liquid ratio. Taking the average depth of the lagoon top water as ~ 0.5m, precipitation levels between 1970-2005 averaging 0.912m per year (Met Office 2006), and an overflow rate of the lagoon to be 35% of the water volume each year, the cumulative volume of liquid water passing through the lagoon per unit area of lagoon would have been 0.912 x 0.35 x 35, approximately an equivalent of 10m^3 or 10,000 kg per m^2. At a 1:30 ratio, this corresponds to ~330kg of tar or a depth of ~0.3m of tar taking the density of the Viscous Tar at 1140kg/m^3 (Xu and Smith, 2005). This correlates well with probings made at the site which indicated a depth of weathered layer of about 0.5-0.7m (based on changes in strength).

Given the reported depth of the lagoon to be ~10m, this indicates weathering at this rate would take another 35 x (10/0.3) = 1150 years to convert the fresh tar to a weathered form. However continued leaching and weathering of the deeper tars will be constrained by the surface weathered tar acting as a barrier. Further leaching will be diffusion limited unless it is possible for the weathered layer to crack and admit either water flow or bulk migration of the underlying tar. The timescale is thus likely to be significantly longer.

Similar effects may be expected around the subsurface circumference of the lagoon if it was located in permeable strata. The groundwater flow rate would affect the initial rate of weathering. However it would eventually become diffusion limited if a similar weathered layer formed at depth. However at this stage it is not possible to state with certainty whether physical and chemical conditions at depth would lead to a similar weathering process. The tar could simply wash away as colloids and soluble matter or could weather and crack leading to fresh tar continually being exposed to groundwater. Further research is needed in this area.

6.5.2.2 Environmental impact

Based on the data in Section 6.5.2.1, and a lagoon surface area of ~11000 m^2 it can be estimated that run off from the surface water lagoon is carrying approximately 2800kg/year of sulfate into the surrounding environment, and 350 kg/year of TOC, based on the weathered green tar 1:10 cascade data. However not all the TOC may be transported. Observations at the lagoon noted a black coating of the colloidal organics around the shore line of the lagoon and on any vegetation at the waters edge.

The impact of leachate on the surrounding environment depends significantly on the physical and chemical nature of the surrounding soils. Sulfate may not be of significant concern, and generated a lower level than the drinking water standard by the end of cascade tests (250mg/L by Council Directive 98/83/EC). pH level remains lower than the drinking water standard

(6.5 by Council Directive 98/83/EC), though this will fall by dilution away from the buffering effects of the main lagoon, and the low surface water pH itself will lead to mobilization of metals and other contaminants along any flow path The organics may be problematical depending on the constituents.

Given the large costs and significant challenges for remediating the source material (Smith et al., 2007), there may be scope for low cost treatment of the surface water using filter systems to handle the acidity, sulfate, and colloidal/soluble organics. Where groundwater contamination is present, then a PRB using similar techniques may be potentially viable

6.5.2.3 Assessment of lagoons

High levels of acidity, sulphate and TOC will be clear indicators of contamination of ground/surface water by acid tars, though the evidence points to the TOC content having a large adsorptive affinity for surface soil and vegetation which may mean it will fall rapidly away from the lagoon. For rapid onsite indicators, a low pH and high conductivity will be strong evidence of acid tar contamination. However attenuation of all three would be considered possible depending on the geochemistry and permeability/porosity of the surrounding environment.

When assessing an acid tar lagoon, it is important to note that the apparently inert and stable forms of weathered tar may give rise to significant leachate levels and should be tested together with the source tar. While batch tests give a clear indication of the likely level of leaching for a particular tar, cascade tests are required to determine long term leaching behaviour, particularly of TOC which remained high for many of the tar types.

6.6 Conclusion and further works

Based on the specific acid tar type tested in this paper the following conclusions can be made:

- Unweathered acid tar leaches significant quantities of acid, sulfate and

TOC both in soluble and colloidal forms.

- Acid tars may weather into a range of different forms depending on the ambient environmental conditions. A model of acid tar weathering has been postulated. However further research is required to confirm and refine it.
- While outwardly seeming stable, all weathered forms of acid tar were capable of leaching reduced, though still significant quantities of acid, sulfate and TOC.
- Cascade tests on all tar types up to a cumulative solid liquid ratio of 1:60 indicated continued production of significant quantities of TOC, while levels of leached sulfate stabilized at this point.
- There is evidence that physical disturbance of the tars influences TOC leaching. Flow cell testing is recommended to provide more realistic conditions and complement cascade tests.
- Acid tars display significant buffering like behavior. This is attributed in part to the large range of organic acids present in the material and part to the diffusion limited processes present in the acid tar-water system.
- It is estimated that acid tar lagoons left unremediated are likely to take centuries to weather to stable forms. Mitigation of the environmental impact is potentially possible but requires further research.

Chapter 7 Flow Cell Leaching of Acid Tars

Hao Xu and Smith Colin

Abstract

Acid tars are a hazardous waste product of the petrochemical refining industry. Past practice included dumping the tars in convenient holes in the ground leading to a potential risk to groundwater. Batch and cascade leaching tests on acid tars have demonstrated that they are capable of releasing mobile components into the aqueous phase, both soluble and in the form of colloids. Such results, however, only reflect the worst case scenario. Batch style tests may significantly overestimate the leaching of acid tars. A set of flow cell tests were therefore designed and carried out to simulate leaching of acid tars over a constrained interface with a saturated model soil. The results demonstrated that the leaching rate of acid tar in flow cell is significantly lower than in batch and cascade test but occurs over a longer term than equivalent cascade test. The tests also demonstrated that acid tars in contact with water can migrate in bulk in a heterogeneous pattern temporally and spatially.

Keywords: acid tar, flow cell leaching test, migration.

7.1 Introduction

Acid Tars are a waste residue of obsolete petrochemical refining processes, comprising a complex mixture of water, sulfuric acid and a large range of organic and inorganic compounds (refer to Nancarrow *et al* 2001 for a detailed background and description of acid tars). Historically, acid tars were dumped into existing excavations or other available sites without proper treatment or an engineered lining system. This has left a legacy of hazardous acid tar lagoons site around the world.

One of the main environmental concerns associated with acid tar lagoons is the potential ground and surface water pollution that may arise when acid tars come into contact with precipitation, surface or groundwater flow. This paper focuses on leaching by groundwater and considers the scenario where the lagoon may be water leached via permeable strata. Batch and cascade leaching tests on acid tars (Xu and Smith, 2007) have indicated a high level of potential leached contaminantion. Acid tars are capable of generating leachate that has low pH and high level of sulfate and Total Organic Carbon (including dissolved organic and organic colloids in suspension), which exceed both the ICRCL 59/83 Trigger Concentrations and the New Dutch List threshold value for soil or groundwater. However, batch and cascade leaching tests typically indicate the worst case scenario by maximizing the tar/water interface. The leaching behavior of acid tars under natural conditions, especially at the base of the lagoon where the main acid tar body is effectively impermeable and the groundwater interacts with acid tars only along a limited interface, is unknown and cannot be directly predicted by batch and cascade tests. Leaching may steadily decline because leached acid tar may weather into a barrier leaving leaching diffusion dominated. Alternatively acid tar may leach and mix into the groundwater. Batch and cascade tests cannot model this.

An alternative flow cell leaching test was, therefore, designed to more closely represent the field situation. Due to the low permeability of acid tar and its viscous nature, which would clog a conventional column leaching test, modifications were required (Hansen, *et al* 2004). The design therefore aimed to simulate long term acid tar leaching along a tar/water interface. The aim of this paper is to describe the flow cell tests employed, to analyze the leaching behavior of acid tars in two flow cells based on both visual assessment and data from monitoring parameters and integrate these findings into a lagoon context. An initial scoping test was carried out in a horizontal flow cell. Following that test a more sophisticated vertical oriented flow cell test was designed and tested. Time constraints meant that it was not possible to repeat the tests. However, the findings indicate unusual behaviour and will be of interest to acid tar lagoon owners (particularly given the severe lack of data on acid tars in the literature).

7.2 Materials and Methods

7.2.1 Acid Tar Samples and Water

The acid tars used in this work were "fresh" viscous acid tar collected from an open upwelling zone from the Hoole Bank acid tar lagoon site (Nichol, 2000). The source tar was produced by oil rerefining. The tar was from the same sample set as used in the batch test reported by Xu and Smith (2007) and is further described in that paper. The viscous tar is a semi-liquid, black colored tar with low pH, high sulfate level and was reported to generate high TOC levels in batch tests (Xu and Smith, 2007).

Purified water processed by an ELGA Option 3 water purifier was used in the test. The purification process removed inorganic components but did not de-ionize the water to simulate clean groundwater.

7.2.2 Model Soil

Permeable strata underlying acid tar lagoons may vary from fractured soil, through gravel to fine sand and sandstone. The current work considered the presumed worst case scenario of fine gravel and coarse sand. This was represented using glass beads, chosen for their general inert properties and transparency, which would assist in flow visualization.

7.2.3 Static Control Test

Prior to the flow tests, control static tests were carried out using beakers (80mm diameter and 100mm height) filled with glass beads of sizes 1mm, 3mm and 5mm. Viscous acid tar was placed on top of both saturated and dry glass beads in a sealed beaker and observed for 7 days to investigate the influence of water on tar migration.

7.2.4 Horizontal Flow Cell

7.2.4.1 Flow Cell

The horizontal flow cell consisted of a 150mm wide by 200mm long by 3mm deep chamber milled into a PTFE base with an acrylic top sealed by an o-ring. The flow chamber was filled by a single layer of 3mm diameter glass beads and a mass of acid tar sample was placed in the middle of the chamber. The inlet water flow was distributed uniformly by an overflow channel on one side of the cell and collected the other side.

7.2.4.2 Water Supply System

The water supply system consisted of a constant water head tank supplying a peristaltic pump. The flow rate during the test was set at 4 litres per day, equivalent to a flow velocity of 0.10mm/s in the central part of the cell.

7.2.4.3 Leachate Collection and Analysis

Leachate samples were collected every 4 hour during the first day and 1 times a day for the remainder of the test. The pH of the leachate was measured by a portable pH meter.

7.2.4.4 Real Time Imaging System

A Canon 350D 8MP digital camera controlled by Canon Remote Capture software was set to capture images of the flow cell every 10 minutes during the first week and every 1 hour for the rest of the test (day 8 to day 36). The camera was located 1m from the flow cell and the camera settings were 18mm focal length, 5.6 aperture and 1/125m shutter speed. The background light was provided by fluorescent lights in the lab.

7.2.4.5 Test Procedure

The test procedure was as follows:

1. Fill the flow chamber with a single layer of 3mm diameter glass beads and then seal it using the transparent window and o-ring. Run the system with purified water for 1 day. Measure the pH of the outlet water as the control data. (2 days before actual test)
2. Drain and disassemble the horizontal flow cell, remove the glass beads and let them dry.
3. Prepare a mass of viscous acid tar sample and place it the middle of the flow chamber. Carefully transfer a layer of glass beads to fill the rest of the space of the flow chamber, seal the horizontal flow cell.
4. Turn on the camera and the controlling PC, and initiate image capture.
5. Turn on peristaltic pump to start water flow.
6. Collect leachate samples and measure the pH periodically.

7.2.5 Vertical Flow Cell

7.2.5.1 Flow Cell

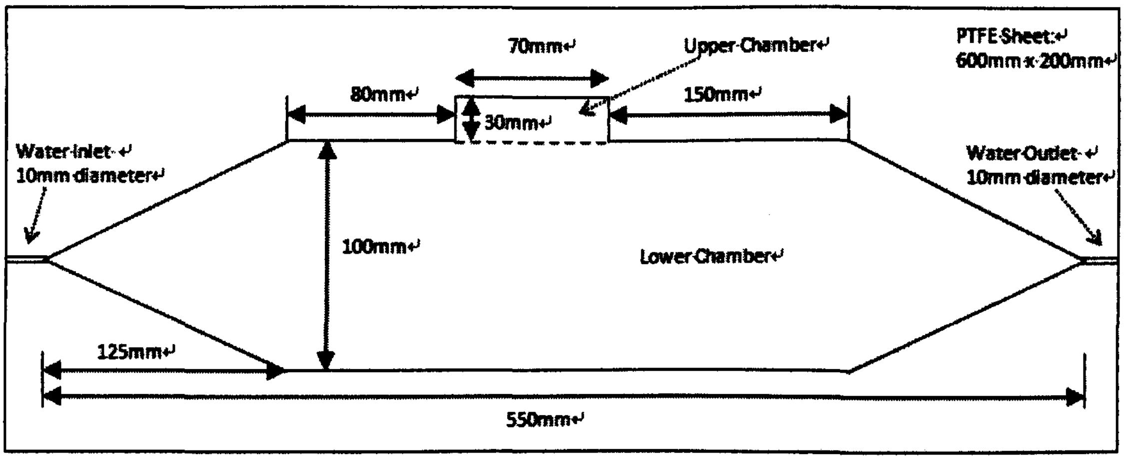


Figure 7-1 Design drawing of flow cell

The flow cell base was formed from a single sheet of PTFE. A 10mm depth chamber was milled into the sheet as depicted in Figure 7-1.The upper chamber was designed to be filled with viscous acid tar, while the lower flow chamber was filled with glass beads as the model soil, as shown in Figure 7-2. The flow cell is mounted vertically in a supporting frame. A glass window covers the front of the chamber and is sealed at the edge using a rubber o-ring. Due to the manufacturing tolerances a small gap was present between the window and the PTFE sheet which is less than 0.1mm. While admitting a minor degree of flow, this was deemed negligible compared to the main flow (less than 1% of the overall flow volume). The chamber was designed in such a shape to produce a uniform flow field adjacent to the tar body.

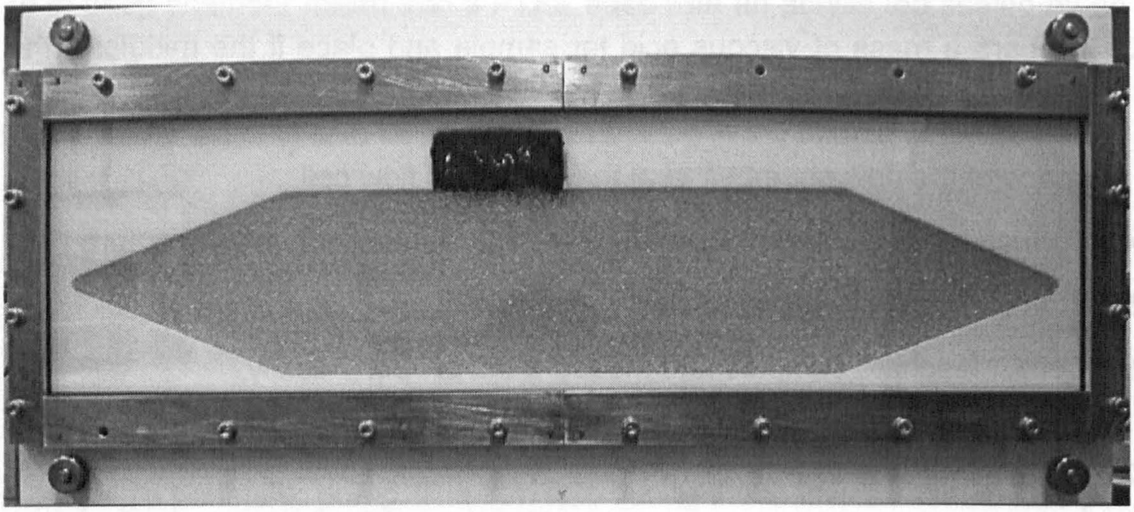


Fig 7-2 Flow Cell

7.2.5.2 Water Supply System

The vertical flow cell test used the same water supply system as was described in Section 7.2.4.2. The flow rate during the test was set at 4 litres per day, equivalent to a flow velocity of 0.074mm/s in the central part of the cell.

7.2.5.3 Real time Monitoring Electrodes and Datalogger

Leachate from the flow cell was connected to 4 flow-through cells each containing an electrode (pH, Conductivity, Dissolved Oxygen and Redox). The voltage signals were collected by an Adept Scientific USB1616FS datalogger and logged by computer every 10 seconds. The data was then converted to real parameters by applying the calibration curve of each electrode. The calibration curve of each electrode was carried out before the control test by measuring standard solutions for each electrode supplied by the electrode manufacturer. The electrodes were connected in parallel, as depicted in Figure 7-3, to avoid cross cell interference.

7.2.5.4 Real Time Imaging System

The same real time imaging system was used as the horizontal flow cell test.

7.2.5.5 Leachate Collection and Analysis

Leachate samples were collected every hour during the first day and 2 times a day for the remainder of the test. The samples were analyzed by DIONEX DX-120 Ion Chromatography (Column type: IonPac CG12A cation exchange column and IonPac AS14A anion exchange column) for inorganic contaminants and SHIMADZU TOC-V CSH TOC Analyzer for Total Organic Carbon (TOC).

7.2.5.6 Test Procedure

The test procedure was as follows:

1. Assemble the empty flow cell. Pour glass beads in through water inlet port, tap the flow cell to settle glass beads until full. Run the system with purified water for 1 day. Collect control water sample and electrodes data. (2 days before actual test)
2. Drain and disassemble the flow cell, remove the glass beads and let them dry.
3. Prepare a viscous acid tar sample by shaping a piece of acid tar using a paper mould into the same dimension as upper chamber of the flow cell and place it in a fridge at 5°C to cool for easier handling.
4. Transfer the shaped acid tar sample into the upper chamber of the flow cell. Apply glass sheet and seal. Pour glass beads in vertically through water inlet port, tilt the cell slightly on the opposite direction of upper cabin so glass beads fell away from tar, tap the flow cell to

settle glass beads until full[1]. Secure flow cell on the support frame and then connect all pipes of system.

5. Turn on the datalogger, logging PC and stabilize all electrodes.
6. Turn the camera on, adjust position and start taking images.
7. Turn on peristaltic pump to start water flow[2].

Note: [1] Despite this some additional settlement of the beads did occur during the test.

[2] It was deemed preferably to saturate the flow cell horizontally with the risk of trapping a small quantity of air. Saturation vertically as a separate stage would lead to water leaching of the acid tar prior to monitoring thus losing initial data. Drilling an air vent hole on the flow cell was also considered but the depth of the milled chamber was so shallow that there was risk of cracking the PTFE sheet.

All experiments were carried out in a constant temperature laboratory at 25°C.

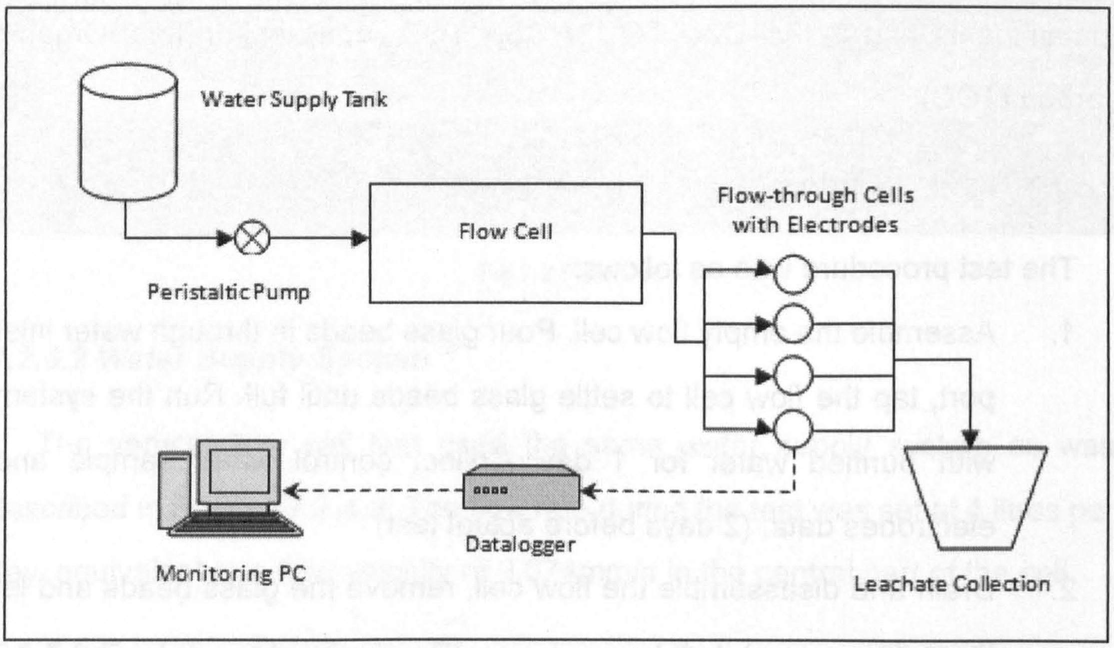


Figure 7-3 Schematic Diagram of Flow Cell Leaching Test

7.3 Results

7.3.1 Static Tests

Images of the control beaker tests (Figure 7-4) indicated that viscous tar was capable of migrating into water saturated glass beads at least as small as

1mm diameter. Such a migration happened in less than one day after the tar sample was placed in the beaker. Under dry conditions, however, migration is minimal, indicating either that water changed the interface tension properties of the acid tar, or that the acid tar partially dissolved in the water.

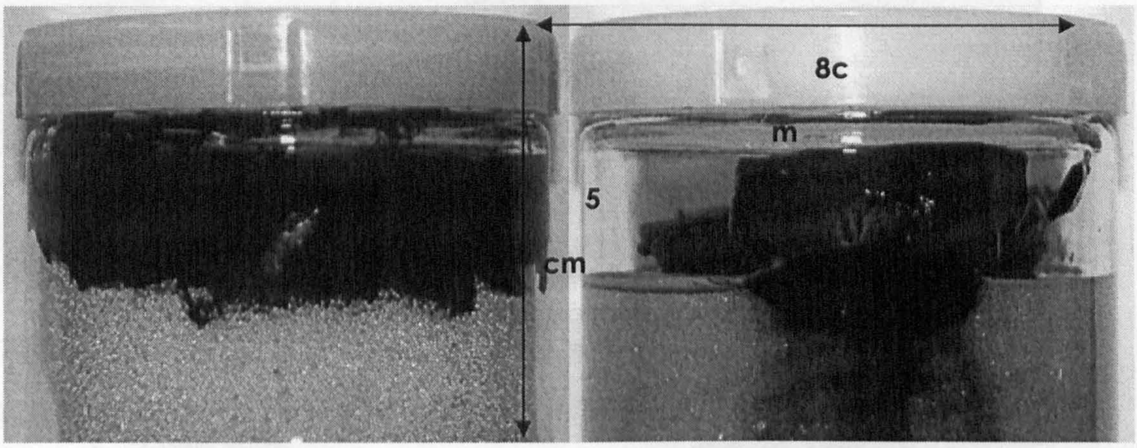


Figure 7-4 Images of 1mm glass beads control beaker test (left: dry; right, saturated)

7.3.2 Horizontal Flow Test

As can be seen in Figure 7-5, a plume was generated after the acid tar contacted the water flow. The plume diminished slowly but never ceased during the test (17 days). Acid tar did not migrate in bulk in this test, but appeared to weather into a more solid form which cracked later in the test on the side towards the water flow. Small particles of acid tar (less than 1mm) were found around the main tar block, as shown in Figure 7-6. Figure 7-7 shows the pH level during the test. The pH level dropped immediately when the water flow reached the acid tar. The pH level fluctuated during the test and showed a trend of slow increase.

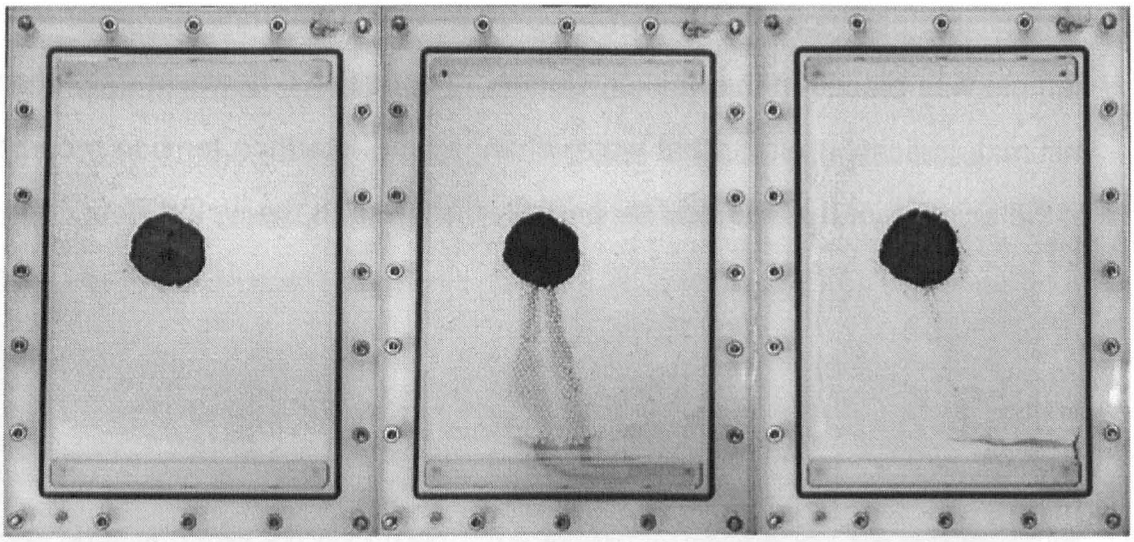


Figure 7-5 Images of horizontal flow cell test, water flow direction: top to bottom.
(Left, before test; center, immediately after acid tar contact with water; right, at the end of test)

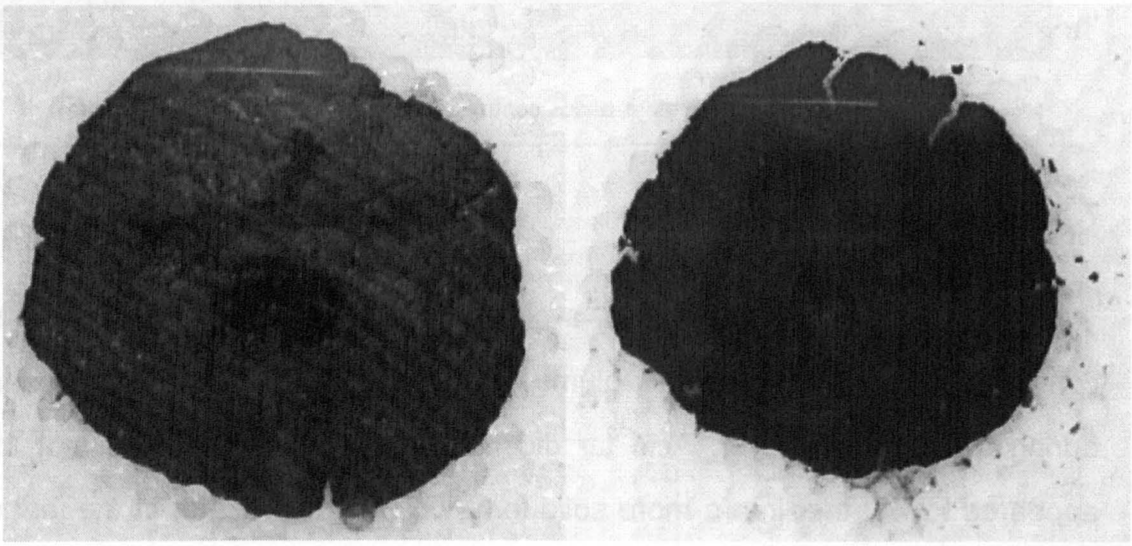


Image 7-6 Cracking of acid tars (left, before test; right, after test)

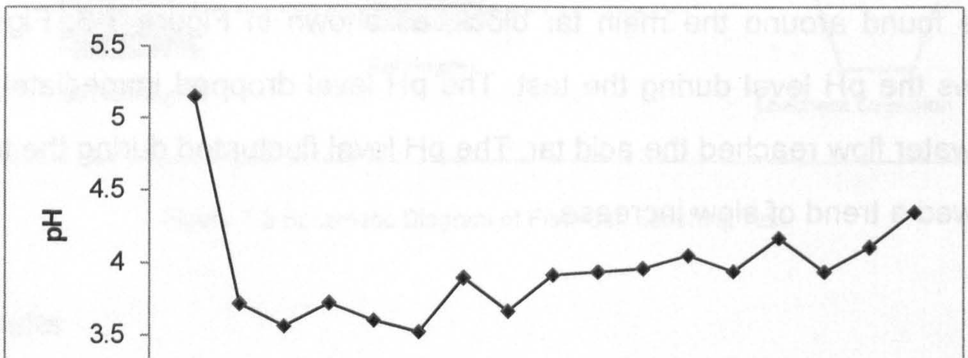


Figure 7-7 pH level of horizontal flow cell test

7.3.3 Vertical Flow Test

7.3.3.1 Imaging Results

The vertical flow cell leaching test was carried out over a period of 36 days. The main visual features of the test were a contamination plume and tar migration. An initial black green colored plume is generated immediately after the inlet water contacts the acid tar, as shown in Figure 7-8(a). After 24 hours, the acid tar sample in the cabinet began to migrate in bulk into the glass beads. The bulk tar migration occurred in discrete stages rather than as a smooth continuous process. In this test 8 stages were identified before the migration stopped, as shown in Figure 7-8(c)-(g). At each stage, acid tar migrates into part of the glass beads in a manner reminiscent of a DNAPL. Such a behavior is further discussed in Section 7.4.3. As fresh acid tar is exposed to the water flow, a plume with increased leachate level is released during each migration. However, the leaching level remains stable at a lower level between migrations. The bulk migration pathways were random, though in this test, most of the pathways were against the water flow direction. It is possible that the settlement of glass beads left a small gap at the top of the flow chamber, which provided an easier route for acid tar migration. However, when compared with the results of the horizontal flow cell test, it can be concluded that the migration is gravity driven. The migration stopped when the upper chamber was empty.

After the test, the flow cell was disassembled. Inspection of the acid tar migration area (Figure 7-9) shows that the migrated tar appeared to be partially dissolved and mixed with the water (Figure 7-10(a)). The system appeared to trap some heavily contaminated leachate. However, inspection after the test showed that this could be rinsed away (Figure 7-10(b), (c)) leaving a residue of larger acid tar particles. The fact that the main water flow during the test did not wash away the more turbid water, indicates some form of weak bonding, or a complete clogging of the pores by the larger particles preventing washout of contaminants in the test.

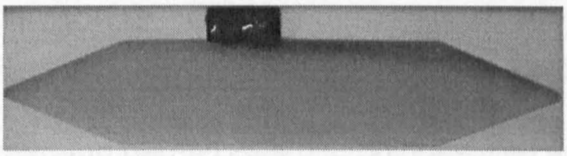
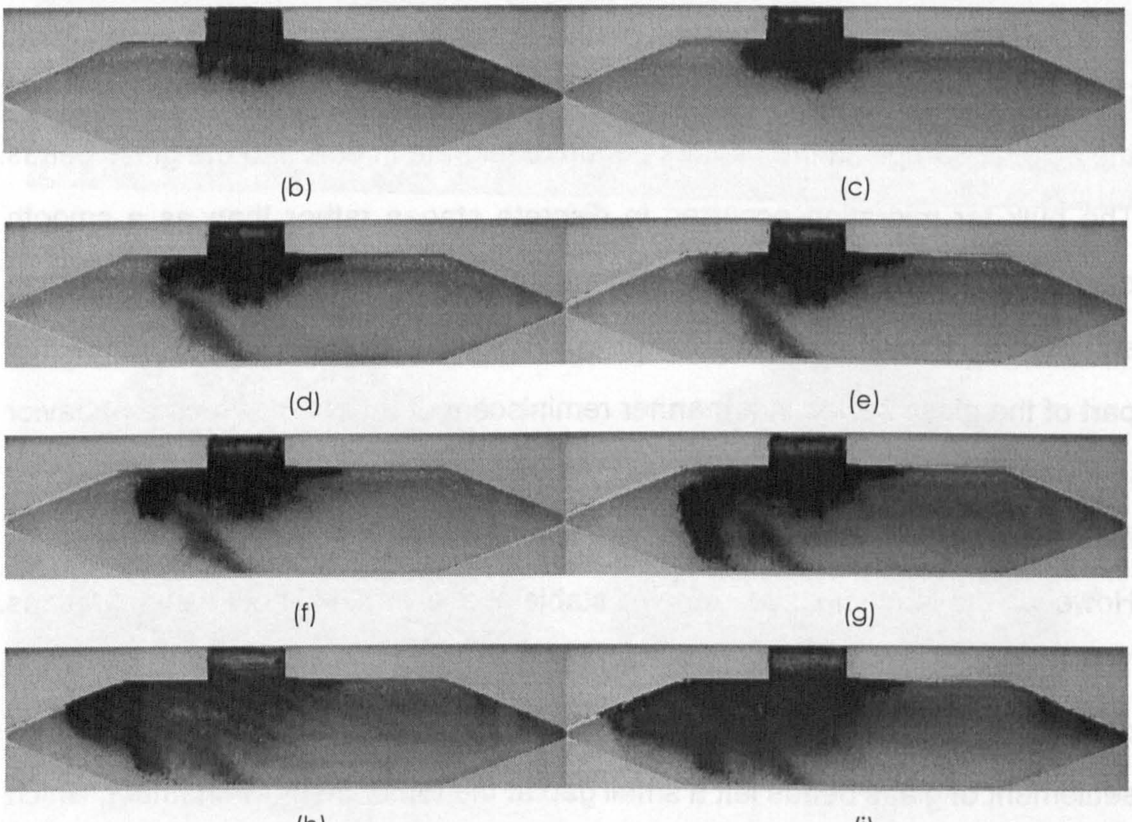


Fig 8 (a) Initial plume immediately after water flow hits fresh acid tar sample.



(b) (c)

(d) (e)

(f) (g)

(h) (i)

Fig 7-8 (b)-(i) 8 staged tar migration. Note: progressive reduction in acid tar level in the upper chamber.

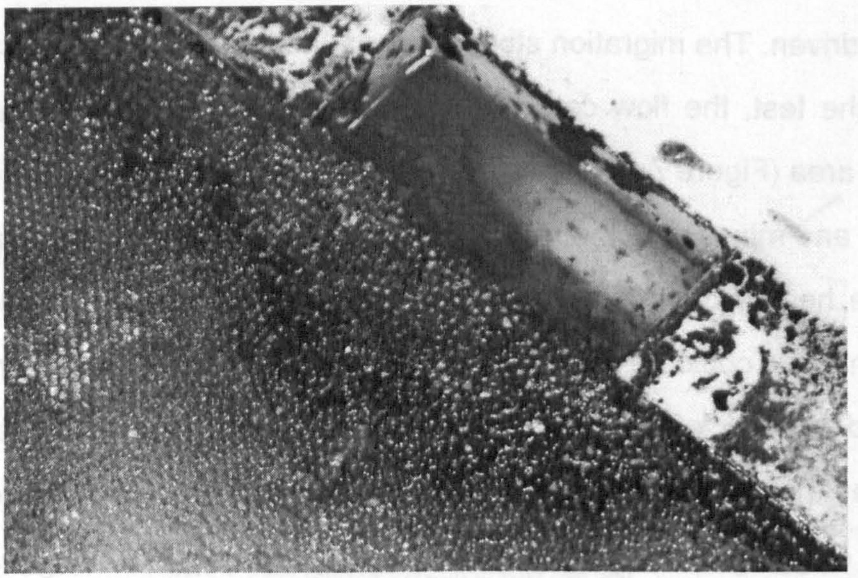


Fig 7-9 Acid Tar migration area after test

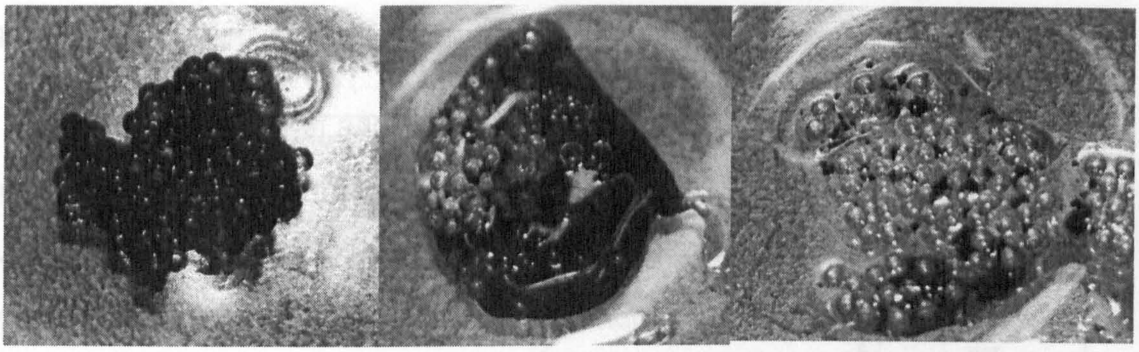
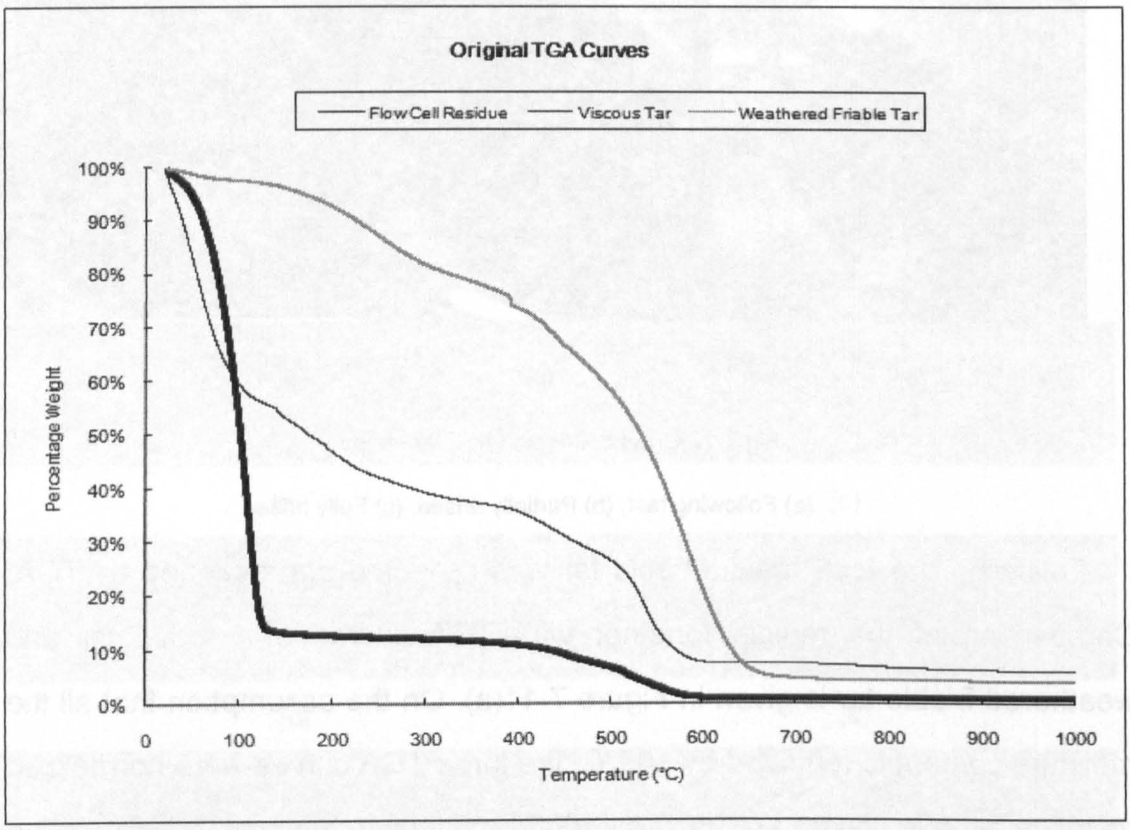

(a) (b) (c)

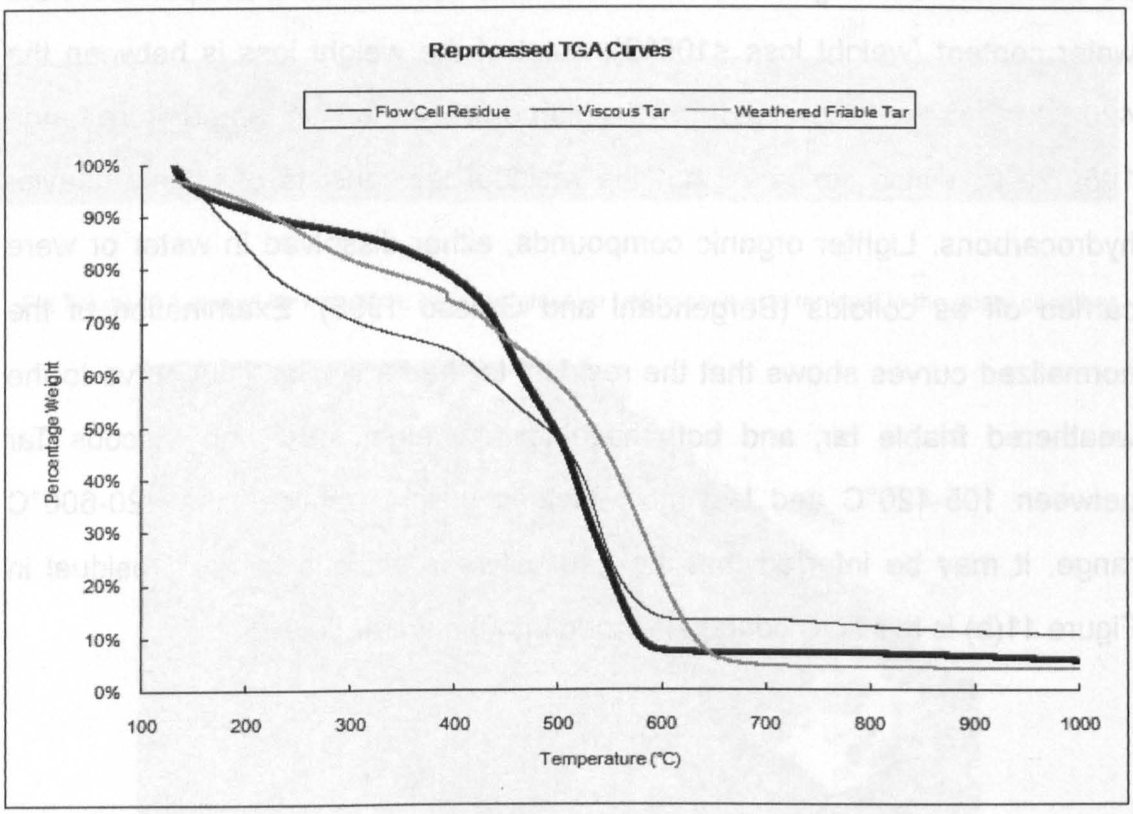
Fig 7-10 Glass beads and acid tar residue

(a) Following test, (b) Partially rinsed, (c) Fully rinsed

Following the test, residual acid tar was collected and scanned by TGA. Comparison of the results together with TGA curves of viscous tar and weathered friable tar is given in Figure 7-11(a). On the assumption that all the moisture content is removed by 105°C, the three TGA curves were normalized by taken sample weight at 105°C as 100%, as shown in Figure 7-11(b). It can be seen from the original TGA curve of flow cell residue that apart from the water content (weight loss <105°C), most of the weight loss is between the 420-600°C range. There is only a fraction of weight loss in temperature range 105-420°C, which indicates that the residual tar consists of mainly heavier hydrocarbons. Lighter organic compounds, either dissolved in water or were carried off as colloids (Bergendahl and Grasso 1998). Examination of the normalized curves shows that the residual tar has a similar TGA curve to the weathered friable tar, and both have lower weight loss than Viscous Tar between 105-420°C and lost most of their weight between the 420-600°C range. It may be inferred that the gap between viscous tar and residual in Figure 11(b) is the TOC content leached into the water flow.



(a) Original TGA curves



(b) Reprocessed TGA curves

Fig 7-11 TGA curve of residue acid tar after flow cell test

7.3.3.2 Flow Chemistry Results

The dissolved oxygen and reduction/oxidation potential electrodes (Redox) returned a stable signal throughout the test. Both D.O. and Redox level are as low as background (purified water). The stable, low level on the two parameters indicates no significant chemical or biochemical reactions occurred during the test.

pH and Conductivity electrode data are plotted against time in Fig 7-12 (a) and (b). The first part of the curve to day 1 is blank data, in which purified water flowed through the system without any acid tar sample. The background level was pH 5.6-5.8 and conductivity almost 0. Once the acid tar sample contacts the water, the pH dropped to 3 and conductivity rose to 1000 µS/cm. The level then stabilized before another peak appears which lower pH to 2.8, the highest acidity during the test and rise conductivity again. This peak correlated to the pulse of tar migration in day 2. Eight similar peaks appeared afterwards until day 22, each correlated to a distinct tar migration event. From day 23 to 36, the pH slowly rose from 4.1 to 5.3 and conductivity stabilized at near 0, bulk acid tar migration also stopped during the period.

The release of water leachable components clearly fluctuates due to acid tar migration. A portion of contaminants is released in a short period of time. Therefore, the pH of the leachate reaches lower level during the migration. Conductivity reflects dissolved contaminants in the leachate and is very sensitive which can be regarded as a simple, indirect parameter of inorganic and water soluble organic contaminants in a leaching test. The results of pH and Conductivity probes correlate well with features discussed in imaging results section.

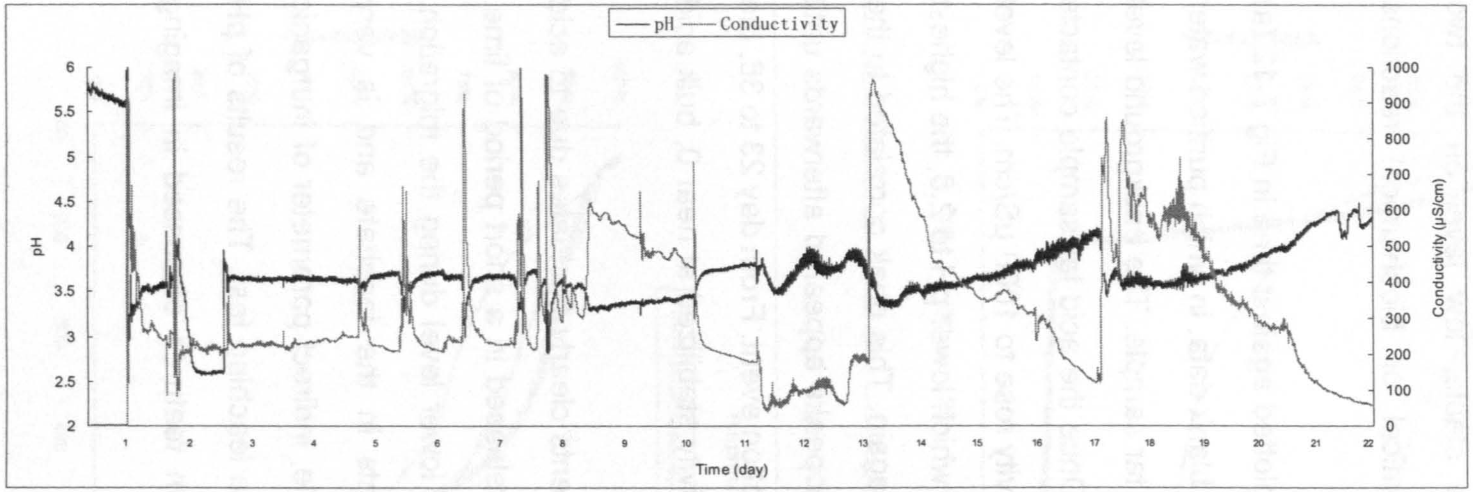


Fig 7-12 (a) pH and Conductivity (day 1 to 22)

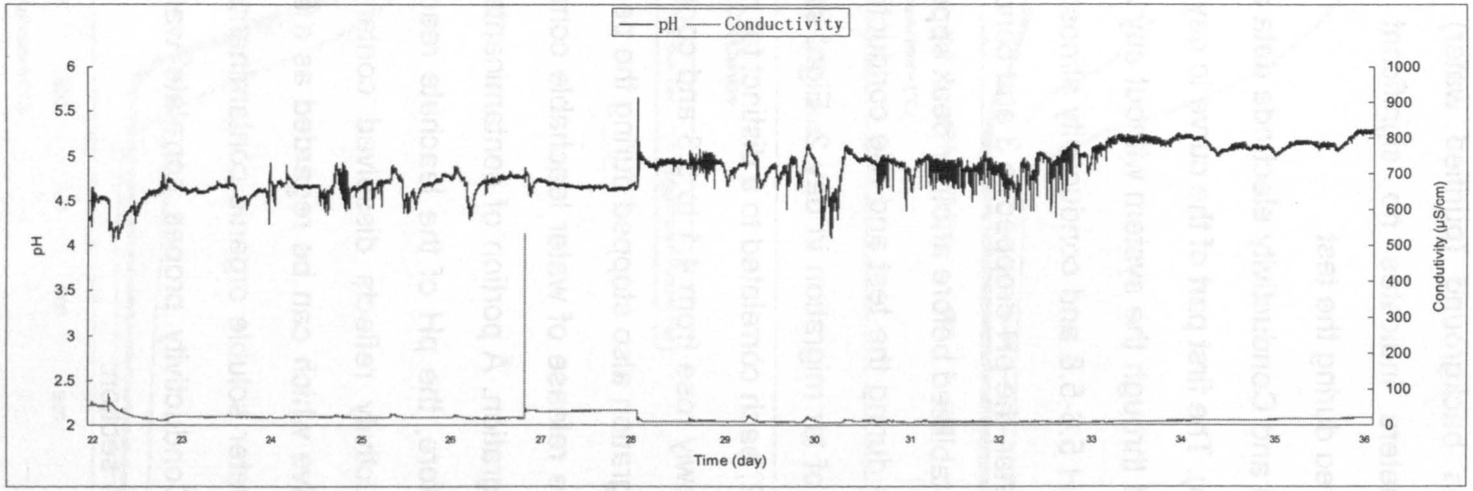


Fig 7-12 (b) pH and Conductivity (day 23 to 36)

7.3.3.3 IC and TOC results

Ion Chromatography analysis of the collected leachate samples show a low level of inorganic components. Sulfate is the inorganic species with the highest level detected by IC and is used as an indicator of inorganic components in the leachate.

Sulfate and Total Organic Carbon results derived from collected leachate samples are plotted in Fig 7-13, as function of cumulative volume of leachate. The leaching is staged but the data is not as detailed as the electrode data because of longer sampling interval. A significant feature is that the sulfate level never exceeds 10 mg/L during the test, which is significantly lower than it in the batch tests.

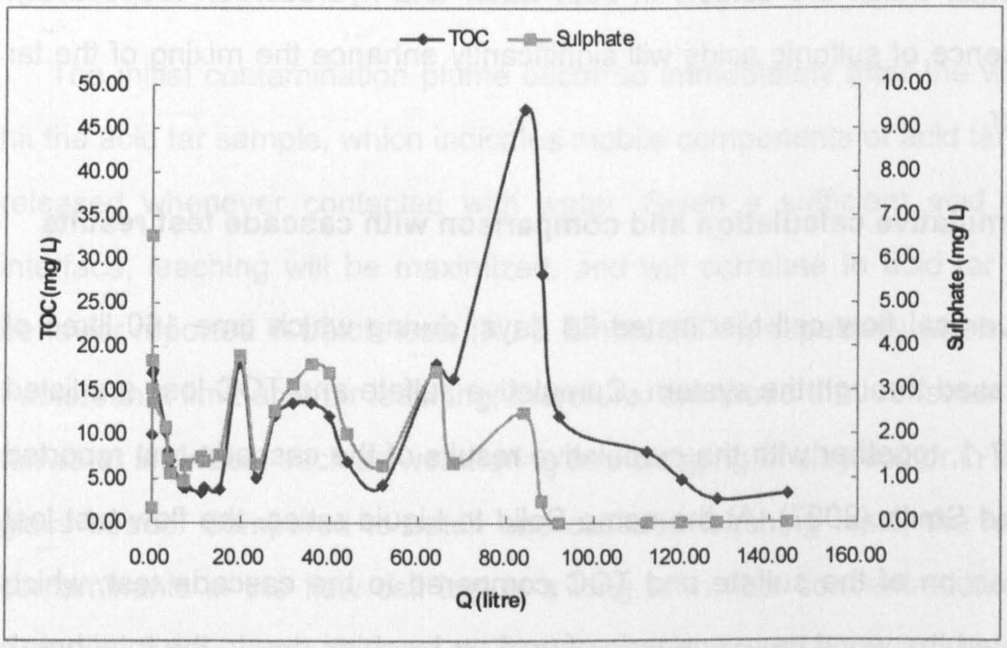


Fig 7-13 Sulfate and TOC

7.4 Discussion

7.4.1 Static Control Test and Horizontal Flow Cell Test

The static control test demonstrates that viscous acid tar was able to migrate into the saturated porous glass beads, while it did not migrate in the horizontal flow cell test. Therefore, it can be inferred that the migration is gravity driven. The static control test also indicates that water is able to enhance the migration ability of acid tar. This may because of the sulfuric acid and organic acids content of acid tars, especially sulfonic acids. Sulfonic acids have both hydrophilic (acid end) and hydrophobic (hydrocarbon end) components, which are soluble in both water and hydrocarbon respectively. The presence of sulfonic acids will significantly enhance the mixing of the tar and water.

7.4.2 Cumulative calculation and comparison with cascade test results

The vertical flow cell test lasted 36 days, during which time 160 litres of water passed through the system. Cumulative sulfate and TOC loss are listed in Table 7-1, together with the cumulative results of the cascade test reported by Xu and Smith (2007). At the same Solid to Liquid ratios, the flow test lost only a fraction of the sulfate and TOC compared to the cascade test, which represented the worst case scenario of acid tar leaching due to the total break down of the acid tar sample during the test. Even the final flow cell cumulative results at a 1:2000 solid to liquid ratio are significantly lower than the cascade test at the 1:50 ratio. With a limited acid tar/water interface, even after the bulk migration, this is expected. The significantly lower overall cumulative sulfate loss compared to TOC loss is assumed to be due to the clogging of void space by residual tar particles discussed in 7.3.3.1 which traps some of dissolvable components (both organic and inorganic) in the less permeable zone, while organic colloids can still be washed away slowly by the water flow. The residual tar taken from the disassembled flow cell was mixed with 10 parts of water per part tar. The IC results for the leachate indicated a sulfate level of approximately 160mg/L. Comparison with the sulfate level for the collected leachate (<10mg/L) and at the end of the cascade tests (<50mg/L), indicates that there is trapped sulfate within the mixture of residual tar and glass beads.

Cumulative Result	Flow Test 1:50	Flow Test 1:2000	Cascade 1:50
Sulfate	0.02%	0.26%	6.05%
TOC	0.07%	2.47%	6.32%

Table 7-1 cumulative results of flow cell and cascade test.

7.4.3 Acid Tar Leaching

The initial contamination plume occurred immediately after the water flow hit the acid tar sample, which indicates mobile components of acid tars can be released whenever contacted with water. Given a sufficient acid tar/water interface, leaching will be maximized, and will correlate to acid tar leaching behavior reported in batch tests (Xu & Smith, 2007), especially when agitated. Factors that limit acid tar leaching, therefore, are those that constrain the acid tar/water interface, such as weathering and clogging of clay/soil or in this case, glass beads. Compared to batch and cascade leaching tests, the release of contaminants in the flow cell test is a long term, low concentration process. Cumulative loss is much lower which means time to stabilization will be over a much longer time scale. Sulfate release is significantly lower than TOC.

One of major issues highlighted by the vertical flow cell test is the migration of acid tar. Migration is staged, and in random directions. Comparison with the horizontal flow cell where no migration occurred indicates that the process is gravity driven. Acid tars that contact with water lose their mobile components, mainly organic solvents. Loss is enhanced by the presence of sulfonic acids and other polar sulfur containing compounds as discussed in Section 4.1

which act like a surfactant. Part of the acid tar thus dissolves and is carried away by the water flow. The remaining residue is solid small tar particles containing mostly heavy hydrocarbons. Such particles clog the void space of glass beads and stop the migration. The fresh tar then has to find another migration pathway to begin another stage of migration. Migration fully stopped when upper cabin was empty and the driving force disappeared.

As indicated in Section 7.3.3.1, the migration of acid tar in the vertical flow cell test is reminiscent of a DNAPL fingering processes into water saturated media. The fingering process is the result of interplay of gravitational, viscous and capillary forces between two immiscible fluids. Both acid tar migration and DNAPL fingering has the following features: (i) The migration is gravity driven; (ii) the migration can be divided into initiation stage, where acid tars begin to migrate into the glass beads and formed protuberances (Figure 8 b,c), and elongation stage, where some of the protuberances developed into primary fingers and secondary fingers (Figure 8 d-i); and (iii) the migration direction is random. However, a key difference is that there is no clear phase boundary between the tar and the water as with a NAPL. Instead the tar appears to absorb water and become more fluid, while retaining a weak sorptive attraction to the glass beads. Figure 7-14 shows a typical NAPL fingering pattern reported by Zhang and Smith (2002). It can be seen that the NAPL fingers have clear phase boundaries compared to acid tar migration. Such a difference may because the acid tar is a complex mixture of sulfuric acid and organic compounds. The presence of sulfuric acid,sulfonic acids and other polar sulfur containing organic compounds renders acid tar more soluble than typical NAPL. Furthermore, the sulfuric acid and organic acids are soluble in both water and the organic components of acid tars, which weakens the phase boundary by acting as an intermediate phase. Therefore, the acid tar/water system is not completely immiscible compared to a typical NAPL/water system and their migration behavior is somewhat different to the NAPL fingering discussed in Section 4.3.

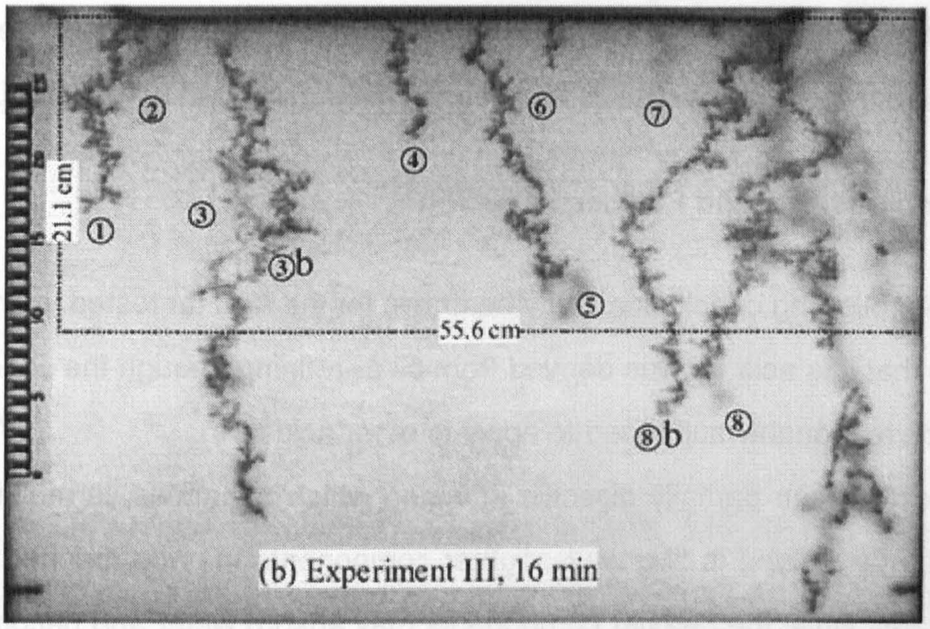


Figure 7-14 example pattern of NAPL fingering (Zhang and Smith, 2002)

Trapped contamination is another consequence of the clogging. Fresh acid tars that contact with water flow quickly lose their organic solvents and weather underwater into solid particles. The clogging of void space by such particles results in a less permeable zone. Inner fresh acid tar can only release mobile contaminants by diffusion, which is significantly slower. Trapped acid tar is not able to release all mobile components when migration fully stops, which is why there is a portion of less leached acid tar remained. The weak binding of acid tar and glass beads may also contributes to the trapping of contaminants.

In natural acid tar lagoons, depending on ground conditions, similar acid tar migration may happen. However, the migration capability of acid tars will be significantly determined by the porosity of the surrounding soil, or the presence of fractures if located on rock. A further issue to be resolved is that of scaling. Is the scale of the migration ‘fingers’ determined by particle size, tar pressure or some other factors? Acid tars can also find easier migration pathways upwelling to ground via cracks or tree root zone. It is possible that if founded on sufficiently permeable media, an acid tar lagoon could slowly migrate into the ground and the more mobile components be washed away. A more likely scenario is that residual tar particles will build up in the pore spaces and clog the soil that forming a partial barrier. A different smeared boundary zone may thus be envisaged of scale determining in part by the pore size of the permeable strata. However, further research is required to confirm this.

7.5 Conclusions and Further Research

The following conclusions may be drawn for the acid tar tested. It should be noted that this acid tar was derived from oil re-refining, though the conclusions may be reasonably supposed to apply to other acid tars.

- Acid tar can partially dissolve in water, which enhances its mobility. This can be viewed in two ways: lighter components may be leached into the water, while the heavier components may absorb water and become more mobile. The acid tar thus may migrate more rapidly in bulk, though loses any clear phase boundary. This phenomenon is attributed to the sulfuric acid and sulfonic acid content, which makes the acid tar more soluble and fluid in water.
- Following continuous leaching a final residue of solid tar particles remains which consists of mainly heavy hydrocarbons with similar properties with Weathered Friable Tar.
- Bulk migration of acid tar appears to be gravity driven. The migration is reminiscent of typical DNAPL fingering migration processes.
- The leaching of acid tar will stabilize at a minimal level when bulk tar migration stops. The clogging of pore space by residual tar particles may trap the more mobile components and further leaching is thus significantly slower. The time scale of such leaching is expected to be months to years based on the model soil.

Further research of acid tar leaching should focus on confirming the migration mechanisms proposed in this paper by carrying out more vertical flow cell tests using different porous media.

Chapter 8 Physical and Chemical Analysis of Acid Tars

Hao Xu and Smith Colin

Abstract

As a waste residue of hydrocarbon refining, acid tars are an extremely complex organic and inorganic mixture possessing unique physical properties. Many of the existing standard analytical methods for contaminated soil or water cannot be directly applied to acid tar samples or leachates. This paper summarizes the modification and development of analytical methods for acid tars during a three year program of research into acid tar lagoons. It outlines the interpretation and integration of data gathered from different analyses to assist in the assessment of the environmental impact of acid tars. TGA analysis is recommended as an initial characterization technique to provide guidance for the subsequent investigation strategy. Analytical methods for viscosity and sulfur related parameters need to be developed by further research.

Keywords: acid tars, density, IC, ICP-AES, TOC, TPH, TGA.

8.1 Introduction

Acid tars are a waste residue of obsolete benzole refining, oil rerefining and white oil production processes. They comprise a complex mixture of water, sulfuric acid and large range of organic and inorganic compounds. Historically, acid tars were dumped into existing holes in the ground, often with various co-disposed materials and without an engineered lining system or pre-treatment. These now form problematic large bodies of contamination as acid tar lagoons. Detailed background information on acid tars may be found in Nancarrow *et al* (2001).

Previous research into acid tar lagoon problems has been limited and has focused mainly on the treatment of acid tars. Analysis of acid tars has mainly focused on its chemical composition. However at present, there is no consistent description of analytical techniques that are most suitable for characterizing acid tars and for assessing acid tar lagoons, both physically and chemically.

This paper focuses on acid tar properties that are most relevant to the environmental impact of acid tars and that are most helpful in understanding the processes that occur in acid tar lagoons. Nancarrow *et al* (2001) lists potential hazardous components of acid tars, which include Polycyclic Aromatic Hydrocarbons (PAHs), phenolic aromatic hydrocarbons, benzene, toluene, ethylbenzene and xylene (BTEX), sulfuric acid, organic acids and other heavy metals and inorganic contaminants arising from co-disposed materials. Xu & Smith, (2007) also suggest that the migration and weathering of acid tars, two distinct characteristics of acid tars, are highly dependent on their moisture content, volatile organic compounds (VOCs), density and viscosity. These properties, therefore, are the targeted parameters that will be discussed in this paper.

Most of the existing literature of acid tar lagoons lists properties of acid tars without describing the analytical techniques employed. Of the few that do discuss analytical methods for acid tars, Nancarrow *et al* (2001) comments: i) due to the extreme chemical complexity of acid tars, the characterization should only focus on objectives of the analysis, e.g. the most mobile compounds of acid tars that pose greater risks to human health; ii) acid tar arising from different production processes have distinct properties that need to be specifically characterized, e.g. acid tars from benzole refining usually have high BTEX levels, while a high acid content should be expected from acid tars arising from white oil production. Nesbit *et al* 1995 suggested that due to the presence of highly sulfonated polar residues which make chromatographic analysis difficult, non-conventional analysis should be used to characterize the nature of acid tars, including: i) class separation by thin layer chromatography/flame ionization detection to separate aromatic hydrocarbons, saturated hydrocarbons and tarry residues; ii) gas chromatography by simulating fractional distillation to produce a boiling point distribution curve; and iii) thermal gravimetric analysis (TGA). However, Nesbit *et al* 1995 proposed the above on a theoretical basis without providing any analytical data. Laboratory data of the work reported in this paper found i) and iii) to be valid but had difficulties in achieving boiling point distributions. This is further discussed in Section 8.2.3.1.

The complexity of acid tar composition and its high sulfuric acid content make the properties of acid tar, both physical and chemical, significantly different from coal tar, NAPLs or any other contaminants. Several existing or standard analytical methods therefore do not work directly on acid tars.

This paper describes the development of an analytical methodology carried out during a program of research into acid tar lagoon parameters for the assessment of the environmental interactions of acid tars. The work was based primarily on acid tars arising from oil rerefining. However, the findings are expected to be applicable to acid tars arising from other processes. Samples considered included viscous tar and various weathered forms: weathered black tar, weathered green tar and weathered black friable tar. Further description of these forms may be found in Xu and Smith (2007). Data of viscous tar and weathered black tar samples are presented as a case study.

8.2 Analysis of acid tars

8.2.1 Physical Properties

8.2.1.1 Moisture Content

Moisture content influences the morphology, physical stability and migration characteristics of acid tars. Acid tars are able to hold water due to their high concentration of sulfuric acid and other organic acids which are hydrophilic compared to coal tars or other organic mixture. Acid tars with a high moisture content are usually more fluid and therefore more mobile. Changes in moisture content also influences weathering processes. Viscous acid tar appears to transform into a range of different weathered forms depending on how it loses water content and organic solvents (Xu and Smith, 2007).

Traditional methods of moisture content analysis usually involve heating the sample in an oven at 105±5°C and uses the weight difference before and after heating to determine the moisture content (British Standard BS812 -109:1990). However, this is not suitable for acid tar samples because acid tars may contain VOCs which may volatilize under 105°C. Heating may also cause acid tars to give off sulfur dioxide (Bukharkina *et al* 1993). To avoid the need for heating and thus minimize emission of sulfur dioxide and VOCs, a silica gel absorption method was used in this research to determine the moisture content. A pre-weighed acid tar sample was placed in a desiccator with silica gel and the weight increase of silica gel (or weight loss of dried samples) after the acid tar sample dried out was used to calculate the water content (detailed procedures are described in Appendix 1). However the silica gel may also absorb VOCs and sulfur dioxide in the gaseous phase (Das *et al*, 2004), and vapours may also occupy the headspace introducing an error. This error can be minimized by limiting the generation of VOCs and sulfur dioxide during the test, by drying the acid tar sample under room temperature and minimizing the head space in the desiccator. Drying time is the key issue in this test. For viscous acid tars using the given procedure, 48 hours of drying was found to be sufficient and the difference between test results of 48 hours and one week drying showed good repeatability (less than 1% difference). The drying time for other types of tar varies depending on their morphology and surface area. Solid lumps of weathered tar did not produce accurate results by this method because of the long drying processes. This may be due to strong binding of water in the tar or due to the low specific surface area of the sample. Due to the typically tough plastic polymeric nature of the weathered material (apart from weathered friable tar) it is difficult to physically break down the tar to increase its specific area. The heterogeneous nature of acid tars will also introduce error and it is recommended that at least 5 tests should be done for each sample to minimize this error. Complementary data may also be provided by TGA tests on the same sample, as discussed later in Section 8.2.4.

8.2.1.2 Density

The modified British Standard 1377: Part 2:1990:7.3 Immersion in water method was used to measure the density of different weathered forms of acid tar. The standard method uses a wax pot to seal a portion of weighed acid tar sample with wax. The cooled wax block is then weighed and immersed into a beaker filled with deionized water, which is placed on a balance, with a string. The balance reading difference before/after the immersion provides the volume of the wax block. By knowing the density of the wax, the density of the acid tar sample can be calculated.

Since unweathered acid tar samples are viscous and hard to handle, the standard method was modified by introducing a small glass container (1.5cm end of a cut 1.0cm diameter test tube). The acid tar sample was first transferred into the weighed container. After weighing the acid tar sample and glass tube, heated liquid wax was carefully poured into the glass tube to avoid trapping air and sealed the sample. The sample was then stringed and immersed into water, as described above. By knowing the density of the glass and the wax, the density of the acid tar sample can be calculated. Control tests of glass containers only were carried out to measure the density of glass, which was compared with supplier data (Pyrex glass). The accuracy and repeatability of this method for acid tar samples with low specific surface area, such as viscous tar and most weathered tars are good. The density of weathered friable tar, which easily breaks into small particles, however, could be slightly underestimated by this method because of its particulate form. Air voids could be sealed by wax and therefore result in a measurement of bulk density rather than particle density. It is recommended to compress weathered friable tar before waxing and tilt the glass tube at an angle when pouring wax to minimize air voids. The detailed test procedure is listed in Appendix 2

8.2.1.3 Viscosity

The viscosity of acid tars determines their ability to migrate. A preliminary kinematic viscosity study was carried out in the laboratory using a viscometer. However, the rapid loss of moisture content and other volatiles from the surface of the acid tar samples tested altered their viscosity and stopped their movement during the test. Further studies were not carried out as part of this research, but a modified method is recommended, such as saturating the air space within the test apparatus with VOCs and moisture from a separated bulk sample of acid tar that is connected to the apparatus air space.

8.2.2 Inorganic and Heavy Metal Analysis

The inorganic components of acid tars consist mainly of sulfuric acid but may also include a large range of co-disposed materials depending on site history. The inorganic analysis of acid tars is relatively straight forward. In this research, Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES) was used as initial screening technique for inorganic and heavy metal contents in acid tars and Ion Chromatography (IC) was used to analyze dissolved inorganic components in the aqueous phase.

8.2.2.1 ICP-AES

Initial screening of heavy metals and inorganic elements of acid tar samples may be carried out using an ICP-AES, a spectrometer that detects electromagnetic radiation of different excited atoms (Skoog, 1992). The standard procedure requires sample to be ashed in an oven at 270°C in order to decompose organic compounds. However, not all organic components of acid tar decompose at this temperature. It was found that the temperature had to be raised to 550°C and maintained for 24 hours to ash the sample completely. At this temperature mercury and lead in the sample would be lost. The heating also causes emission of sulfur dioxide. Thus the sulfur content by ICP will not be accurate and should not be relied upon. The ashed samples are then digested by concentrated nitric acid prior to the ICP analysis.

ICP-AES can identify 30 elements, Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, V, Zn. It is a good screening technique for acid tars, which will give indication of most of the possible heavy metals and inorganic components in acid tars.

8.2.2.2 pH and Ion Chromatography (IC)

High acid content is one of the most distinct features of acid tars and is related to the leaching and weathering processes of acid tars. pH is a good parameter that reflects the total acidity of acid tar leachates, which comprises sulfuric acid, sulfonic acids and carboxylic acids (Frolov *et al,* 1981). pH of acid tar leachates may be directly measured using standard methods.

IC may be used to measure dissolved inorganic ions in acid tar leachates. The IC analyzer (DIONEX DX-120) used in this PhD is capable of detecting 12 cations and anions in the aqueous phase, which are anions: Fluoride, Chloride, Nitrite, Bromide, Nitrate, Phosphate, Sulfate and cations: Sodium, Ammonium, Potassium, Magnesium and Calcium. The DX-120 uses a conductivity detector. For cation detection, a 250mm IonPac CG12A is used as the guard column and a 4*250mm IonPac CG12A cation exchange column is used as the analysis column. The eluent for cation separation is 20mM methane sulfonic acid and the pH is buffered at 1.70. For anion detection, a 250mm IonPac AS14A is used as the guard column and a 4*250mm IonPac AS14A anion exchange column is used as the analysis column. The eluent for anion separation is 8mM Na_2CO_3 and 1.0 $NaHCO_3$ buffering solution and the buffered pH is 10.80. The calibration for the DX-120 is a 5 point linear calibration and the standard solution used is produced by Fisher Scientific, catalog number J/452/05 (Anion) and J/4554/05 (Cation). The separation time and concentration of the standard is listed in Table 8-1. IC is a quick, accurate method, capable of detecting most of the common inorganic compounds that acid tar leachate contains, especially sulfate, the most dominant inorganic components of acid tars. A detailed analysis procedure is listed in Appendix 4. The only modification of the method with respect to acid tars is that due to the extremely high concentration of sulfate and acidity in some leachates. The leachate may require dilution 10 to 50 times before IC analysis depending on the estimated sulfate concentration.

Figure 8-1 shows sample peaks for IC analysis on one acid tar leachate sample. For cations, there were five significant peaks detected, all at a relatively low concentration. For anions, sulfate was the only significant peak and all other peaks were less than one tenth of the sulfate level. The negative peak appearing prior to 2 minutes was water, a typical feature of IC diagrams. It should be noted that the DX-120 used in this PhD is designed for detecting the inorganic ions listed above only and the maximum retention time is 15 minutes. While it is possible that other inorganic ions or polarized organic compounds may appeared as a peak in the diagram, the DX-120 could not identify them because the lack of standards. All the IC traces from the analysis of acid tar leachate samples did not show any significant unidentified peak within 15 minutes. Therefore, it can be concluded that there were no unidentified ions of significant level in the acid tar leachate.

Ion	Retention Time (m)	Concentration (ppm)				
Cation (Fisher Scientific J/4554/05)						
Sodium	2.950	1.25	2.50	6.25	12.50	25.00
Ammonium	3.300	3.50	7.00	17.50	35.00	70.00
Potassium	4.000	2.50	5.00	12.50	25.00	50.00
Magnesium	6.100	2.00	4.00	10.00	20.00	40.00
Calcium	7.600	3.88	7.75	19.39	38.77	77.54
Anion (Fisher Scientific J/452/05)						
Fluoride	2.400	1.21	2.43	6.025	12.15	24.30
Chloride	3.400	4.00	8.00	20.00	40.00	80.00
Nitrite	4.000	2.50	5.00	12.50	25.00	50.00
Bromide	5.000	6.00	12.00	30.00	60.00	120.00
Nitrate	5.500	5.00	10.00	25.00	50.00	100.00
Phosphate	7.400	11.30	22.60	56.50	113.00	226.00
Sulfate	7.900	7.90	15.80	39.50	79.00	158.00

Table 8-1 Standard solution for DX-120 Ion Chromatography

Table 8-2 (a) and (b) present the raw data from the 1:10 batch leaching test results of various tar samples and their mean and relative standard deviation. It can be seen that most of the results showed adequate repeatability though some of the relative standard deviations are significant, especially for sulfate. Such deviation is a result of the heterogeneous characteristic of acid tars. The distribution of water, sulfuric acid, inorganic components and organic components is not homogeneous even within a small sample from which the leachate is generated. Higher sulfate deviation may be primarily due to the influence of organosufur compounds including organic sulfate and possible sulfonium ions discussed in Section 4.1.2, which forms an equilibrium with sulfate ions in the aqueous phase. The equilibrium is very sensitive to even small changes in , e.g. temperature or pH.

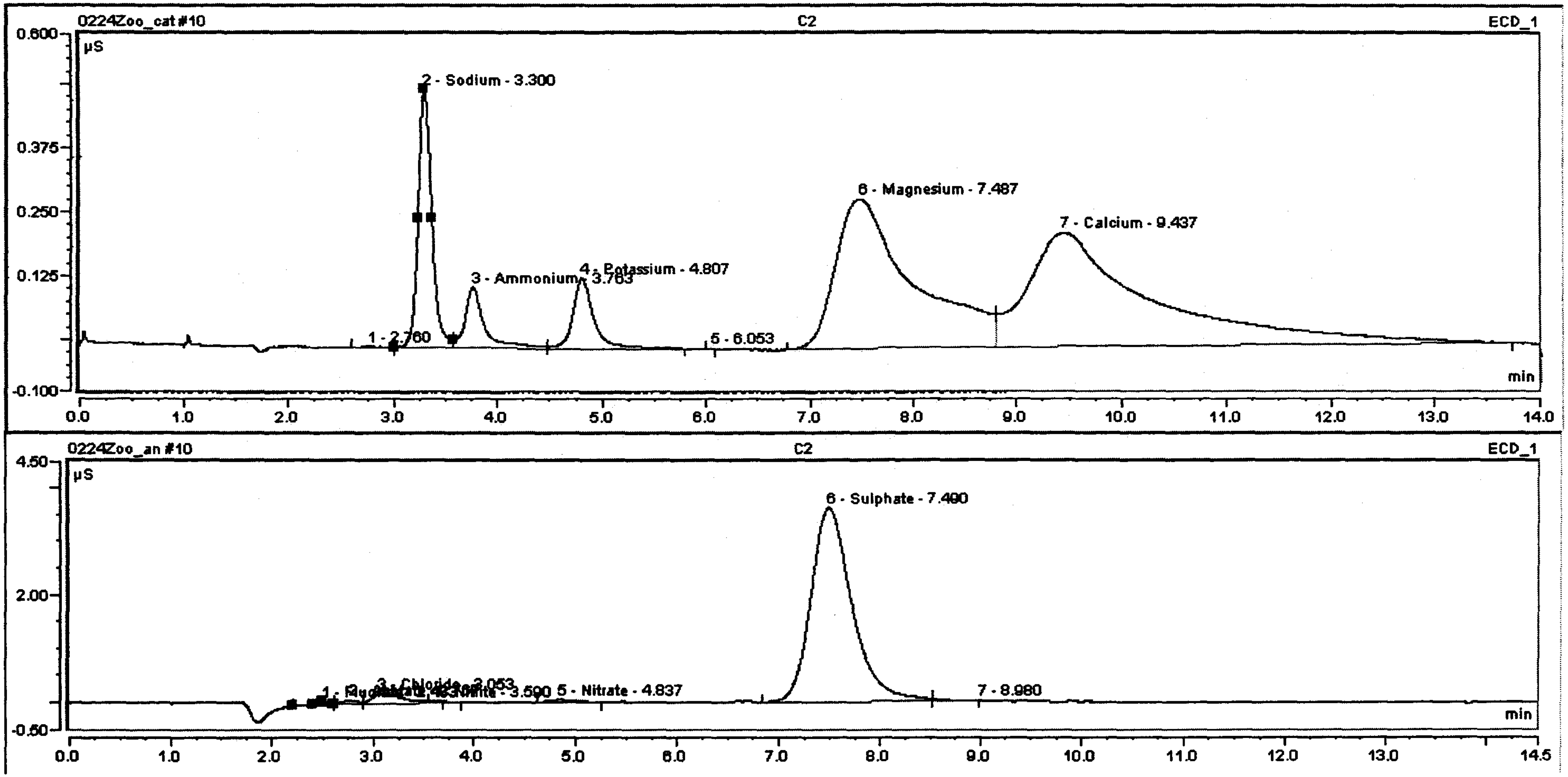


Figure 8-1 Sample peaks from IC analysis of an acid tar leachate sample

Concentration (mg/L)	Sodium	Potassium	Magnesium	Calcium	Chloride	Phosphate	Sulphate
Viscous Tar 1	26.84	21.00	146.24	19.54	32.82	230.17	1422.21
Viscous Tar 2	28.56	19.41	150.75	21.39	30.81	237.92	1438.89
Viscous Tar (acidic smell) 1	37.61	38.68	336.56	12.51	40.43	221.04	8381.33
Viscous Tar (acidic smell) 2	37.76	40.58	344.17	13.77	36.74	225.49	8347.49
Weathered Friable Tar 1	24.03	13.15	151.09	17.62	26.00	275.09	1187.66
Weathered Friable Tar 2	25.98	12.79	148.46	16.64	27.67	270.93	1191.32
Weathered Black Tar 1	32.42	11.51	86.99	230.73	20.00	274.59	1429.37
Weathered Black Tar 2	34.46	12.16	84.34	224.26	22.63	278.20	1454.46
Weathered Green Tar 1	84.25	20.47	125.18	109.83	19.92	229.04	2869.56
Weathered Green Tar 2	85.16	21.80	128.60	113.47	18.19	225.95	2818.97
Weathered Black Tar (alternative location) 1	89.10	27.28	173.03	219.94	22.70	215.52	2916.52
Weathered Black Tar (alternative location) 2	86.36	28.98	167.30	219.01	20.29	220.01	2945.41

(a) Sample IC results

Concentratiion (mg/L)		**Sodium**	**Potassium**	**Magnesium**	**Calcium**	**Chloride**	**Phosphate**	**Sulfate**
Viscous Tar	*mean*	27.7	20.20374	148.4956	20.46489	31.81415	234.0453	1430.5484
	standard deviation	5.34%	6.28%	6.85%	8.36%	6.36%	12.83%	9.72%
Viscous Tar (acidic smell)	*mean*	37.6838	39.62864	340.3641	13.14113	38.58131	223.2669	8364.4117
	standard deviation	0.03%	4.54%	8.50%	6.06%	17.63%	4.44%	6.84%
Weathered Friable Tar	*mean*	25.005	12.97	149.775	17.13	26.8371	273.0075	1189.4912
	standard deviation	7.60%	0.50%	2.31%	2.80%	5.17%	3.17%	0.56%
Weathered Black Tar	*mean*	33.44	11.835	85.665	227.495	21.3121	276.3949	1441.9111
	standard deviation	6.22%	1.78%	4.10%	9.20%	16.21%	2.37%	21.83%
Weathered Green Tar	*mean*	84.705	21.135	126.89	111.65	19.05577	227.4948	2844.2688
	standard deviation	0.49%	4.18%	4.61%	5.93%	7.78%	2.11%	45.00%
Weathered Black Tar (alternative location)	*mean*	87.73	28.13	170.165	219.475	21.49208	217.7648	2930.9623
	standard deviation	4.28%	5.14%	9.65%	0.20%	13.47%	4.65%	14.24%

Table 8-2 (b) means and relative standard deviation of results in (a)

Charge balance is another important factor in IC analysis. Although a high quality analysis of groundwater in which all the important species are determined should have charge balance of ±5%, it is unlikely that the charge balances of leachates containing complex organic mixtures would be so good because of the large dilution factor and that not all species are determined (Channer *et al*, 1999). The leachate analysis by Channer *et al* had charge balances (in terms of Q+/Q-, Q refer to the charge of anions or cations) of 0.2 to 2.8. Steinmann and Shotyk (1997) reported IC analysis of sulfur and ions in pore water from the Jura Mountains, Switzerland and suggested that the charge balance is influenced by pH, redox state and organic species in the aqueous phase.

For acid tars, the charge balance is highly influenced by dilution, pH and high levels of sulfur containing organics. Table 8-3 lists the charge balance of acid tar leachate data presented in Figure 8-2a. The charge balance is presented in units of mMol/L total positive/negative charge. The charge of sulfate is highly sensitive to the pH of the leachate. For leachate with pH lower than 1.9, the sulfate is in form of HSO_4^- and therefore contribute 1 negative charge per ion. For leachate with pH higher than 1.9, the sulfate is in form of SO_4^{2-} and contribute 2 negative charge per ion. Similarly, phosphate has a three phase dissolution process and in acidic solution it is mainly in forms of H_3PO_4 or $H_2PO_4^-$, which contribute 0 or 1 negative charge per ion respectively. In acid tar leachates, phosphate contribute to only a fraction of the total negative charge and sulfate is the only dominant anion in the solution. The concentration of hydroxide (OH^-) is negligible at low pH and is therefore ignored. For cationic charge, hydrogen ion is included because of the acidic environment. Magnesium and calcium are the dominant cations identified by IC. In addition, iron and aluminum identified by ICP-AES analysis also contribute to a small potion of cations in the leachate. The resulting charge balance data showed excessive anion (sulfate), which may be caused by the following reasons:

a) Over estimation of inorganic sulfate by IC

Over estimation of inorganic sulfate by IC may due to the pH difference of the IC eluents and the presence of organic sulfate. The eluent pH for cation analysis is 1.70 (methane sulfonic acid) and 10.80 for anion analysis (Na2CO3 and NaHCO3 buffer). As discussed in the sulfur chemistry section, the production of acid tars involved addition of sulfuric acid to alkenes, as described in Figure 4-3, which produce organic sulfate and the reaction is an equilibrium. During the cation analysis with pH 1.70, the acidic environment will not significantly affect the equilibrium. However, during the anion analysis with pH 10.80, the alkaline environment will push the equilibrium towards the left side, encourage the ionization of organic sulfur, releasing associated sulfate ions. Therefore, the high pH variation between cation and anion analysis may result in the overestimation of sulfate ions in the acidic solution, and it is more likely that this is the primary reason for the charge inbalance.

b) Undetected positive organic ions

Another source of excessive anions may caused by undetected positive organic ions, such as sulfonium ions discussed in sulfur chemistry section. The ionized organic ions are usually quite large and therefore have much longer retention time than inorganic ions. The DX-120 is programmed to identify inorganic ions in a solution and the maximum retention time is 15 minutes per sample. The large organic ions may not be able to travel through the column in time to be detected by the conductivity detector.

c) Unidentified inorganic species

The cation deficit of acid tar leachates may also be caused by unidentified inorganic species by IC or ICP-AES. One possible example is lead, which can not be identified by IC and will evaporate during the ICP-AES high temperature sample preparation process discussed in section 8.2.2.1. Such possibilities should be noticed and addressed in further research.

Charge (mMol/L)	pH	Anions	Cations	Excessive anions	Q+/Q-
Viscous Tar 1	2.25	32.03	22.69	9.34	0.71
Viscous Tar 2	2.32	32.46	22.36	10.11	0.69
Viscous Tar (acidic smell) 1	1.66	87.25	55.07	32.18	0.63
Viscous Tar (acidic smell) 2	1.62	86.90	57.93	28.97	0.67
Weathered Friable Tar 1	2.34	27.62	23.04	4.58	0.83
Weathered Friable Tar 2	2.4	27.66	22.26	5.39	0.80
Weathered Black Tar 1	3.27	32.65	24.75	7.90	0.76
Weathered Black Tar 2	3.32	33.21	24.26	8.95	0.73
Weathered Green Tar 1	2.34	62.16	26.45	35.70	0.43
Weathered Green Tar 2	2.24	61.07	28.17	32.90	0.46
Weathered Black Tar (alternative location) 1	2.45	62.99	34.12	28.87	0.54
Weathered Black Tar (alternative location) 2	2.45	63.64	33.53	30.11	0.53

Table 8-3 Charge balance of acid tar leachate data presented in table 8-

8.2.2.3 Sulfuric Acid Content and Total Sulfur Content

Determination of the sulfuric acid content and total sulfur content of acid tars was found to be highly challenging. The acidity of acid tars is primarily due to sulfuric acid, sulfonic acids and carboxylic acids (Frolov *et al,* 1981). Therefore, the sulfuric acid content cannot be determined by pH. The sulfate level could be used to estimate the sulfuric acid content but this will be overestimated because sulfate may also exist in forms of other mineral salt, e.g. $CaSO_4$. The sulfur content of acid tars exists in forms of sulfur dioxide, sulfate and organic sulfur. As discussed in Section 8.2.2.1, ICP analysis will underestimate total sulfur content and IC analysis can only measure sulfate. Therefore, if total sulfur content is required, an alternative analytical technique needs to be developed. One of the main impacts of acid tar arising from the sulfuric acid content is emission of sulfur dioxide gas, while this was not determined in the current work.

8.2.3 Organic Analysis

Organic analysis of acid tars is significantly more complicated than inorganic analysis. Acid tar contains such a large range of organic compounds. At present no single instrument can identify each one. The organic species of acid tars can be summarized into 3 major groups, as shown in Table 8-4.

Categories	Possible Compounds
Volatile Organic Compounds	Benzene, Toluene, Ethylbenzene and Xylene (BTEX) etc.
Petroleum Range Organics	C5-C35, Aliphatic and Aromatic Organics. Possible species: Phenolic organics, PAHs, Sulfonic hydrocarbons[1]
Heavy Organics	Asphaltenes, paraffins and naphthenes.

Table 8-4 Organic Composition of Acid Tars

(Nancarrow *et al*, 2001, Milne *et al*, 1986, Frolov *et al*, 1981)

[1] The acid tar is produced by a sulfuric washing process, which uses highly concentrated H_2SO_4. The unsaturated hydrocarbon and sulfur contained hydrocarbons can be sulfonated by H_2SO_4 and dissolved in the sulfuric acid. The organic species of acid tars, therefore, will contain a large portion of sulfonic hydrocarbons ($R\text{-}SO_2\text{-}OR'$, where R and R' represents aliphatic or aromatic organics), especially in the petroleum range. (Claxton, 1961)

8.2.3.1 Toxic Compound Screening

Of the three categories of organic compounds contained in acid tars, heavy organics are considered to pose limited risk to human health (the main hazards will be direct contact and ingestion) and the environment because they are mostly inert and immobile. VOCs and petroleum range organics, especially BTEXs, phenolic organics and PAHs, are toxic and mobile components of acid tars that need to be identified.

Following Florez Menendez *et al* (2000), static headspace was used as a sampling technique for Gas Chromatography - Flame Ionization Detector (GC-FID) BTEX analysis. Acid tar samples were placed in a sealed glass container for 48 hours to allow VOCs to saturate the head space of the container. The head space was then sampled by a syringe and submitted for GC-FID analysis.

Phenolic organics may be analyzed by High Performance Liquid Chromatography (HPLC) following procedures described by British Standard: BS 8855-2:2000. 16 priority PAHs may be analyzed by Gas Chromatography Mass Spectrometry (GC-MS) following procedures described by British Standard DD8855-1:1999.

In this research, GC-FID screening simulating fractional distillation, as suggested by Nesbit *et al* (1995) proved to be unsuccessful due to the high number of organic compounds in acid tar, the resulting peaks in the chromatogram that overlap with each other which makes it impossible to identify them. The organic analysis of acid tars thus has to be categorized into targeted groups.

8.2.3.2 Total Petroleum Hydrocarbon (TPH)

TPH is a parameter that reflects hydrocarbon concentration in the C5-C35 range, including both aliphatic and aromatic hydrocarbons. It is a useful measure of organic contamination for soil and heavily contaminated water (Kiely G. 1998). In this research, the hexane extraction gravimetric method was used to determine TPH values (USEPA Method 1664 1995, Onianwa P.C 1995). Detailed procedures are described in Appendix 5. It was found that the method worked well with viscous acid tars, however weathered forms of acid tars showed zero results after the solvent was evaporated. This is possibly because it is hard to extract TPH from solid weathered tars that have limited surface area (weathered black tar) or the TPH content had been leached during the weathering process (weathered friable tar).This issue is further discussed in the case study. Following extraction a GC-FID test could be used to screen detailed compounds of TPH, though this was not carried out in this research.

8.2.3.3 Total Organic Carbon (TOC)

TOC is used as a measure of the organic level of leachate in leaching tests of acid tars. The level reflects not only dissolved organic compounds, but also organic colloids that formed during the agitation in leaching tests (Bergendahl and Grasso, 1998), which can pass through 0.45µm filter paper. Since most of the organic compounds in acid tar samples used in this research are not soluble in water, it is considered that colloids are the major source of TOC. The TOC, however, is still a good measure of organic contamination of acid tars in aqueous phase because organic colloids are equally likely to form in natural conditions.

8.2.4 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis measures the weight loss of a sample in relation to temperature changes (Haines, 1995) and provides additional data that can assist in understanding the distribution of organic and inorganic components of acid tars. Comparison of TGA curves from different weathered forms of acid tars also provides insight into the weathering process.

The TGA can be carried out using nitrogen (inert) or oxygen (reactive) as purge gas. In the presence of oxygen, organic compounds will be oxidized releasing carbon dioxide, water vapour and other gases. TGA using oxygen as the purge gas typically aims to study the combustion characteristics of the analyte. TGA using nitrogen as the purge gas studies the thermal behavior of organic compounds based on their boiling point or decomposition temperature, which can be used to estimate the molecular weight distribution and is more appropriate for this study. When heated in a nitrogen environment, organic compounds will evaporate or decompose depends on their boiling point or decomposition temperature. Therefore, although not able to give direct information of how different sized hydrocarbons are distributed in an acid tar sample, TGA can indicate the distribution of compounds of acid tar samples by molecular weight and it gives fairly accurate information of moisture content, and inorganic residue. The cross-validation of TGA data with data from other methods and the comparison of TGA data of different acid tar samples can also provide information of how hydrocarbons are distributed differently in fresh and weathered acid tars.

The controlling parameters in TGA analysis are primarily the temperature program and rate of heating. Temperature programs investigated in this research included 20-1000°C scanning and grid temperature scanning at each hundred degrees (scanning of 20-100°C, isothermal for 30 minutes, scanning of 100-200°C, isothermal for 30 minutes etc). The heating rates investigated in this research included raising the temperature at 10°C per minute and 20°C per minute. Figure 8-2 shows the comparison of TGA curves using scanning and grid temperature programs at 10°C or 20°C per minute heating rate. The resulting scanning curve at 10°C C/minute heating rate was very similar to the grid curve at 20°C/minute, while had lower weight loss than the grid curve at 10°C/minute at all temperatures. Such results indicated that the lower heating rate gives sufficient time for organics to evaporate (or decompose) at their evaporation (or decomposition) temperature and the grid program also allows more organics to escape than scanning program because of the much longer running time contributed by the isothermal stages (450 minutes longer than scanning program per test). However, the grid curves did not show any significant difference in pattern compared to the scanning program. Furthermore, scanning is the most common TGA program applied to organic mixtures, e.g. TGA results for coal tar pitches shown in Figure 8-3. Therefore, 20-1000°C scanning at 10°C/minute was deemed appropriate for acid tar analysis.

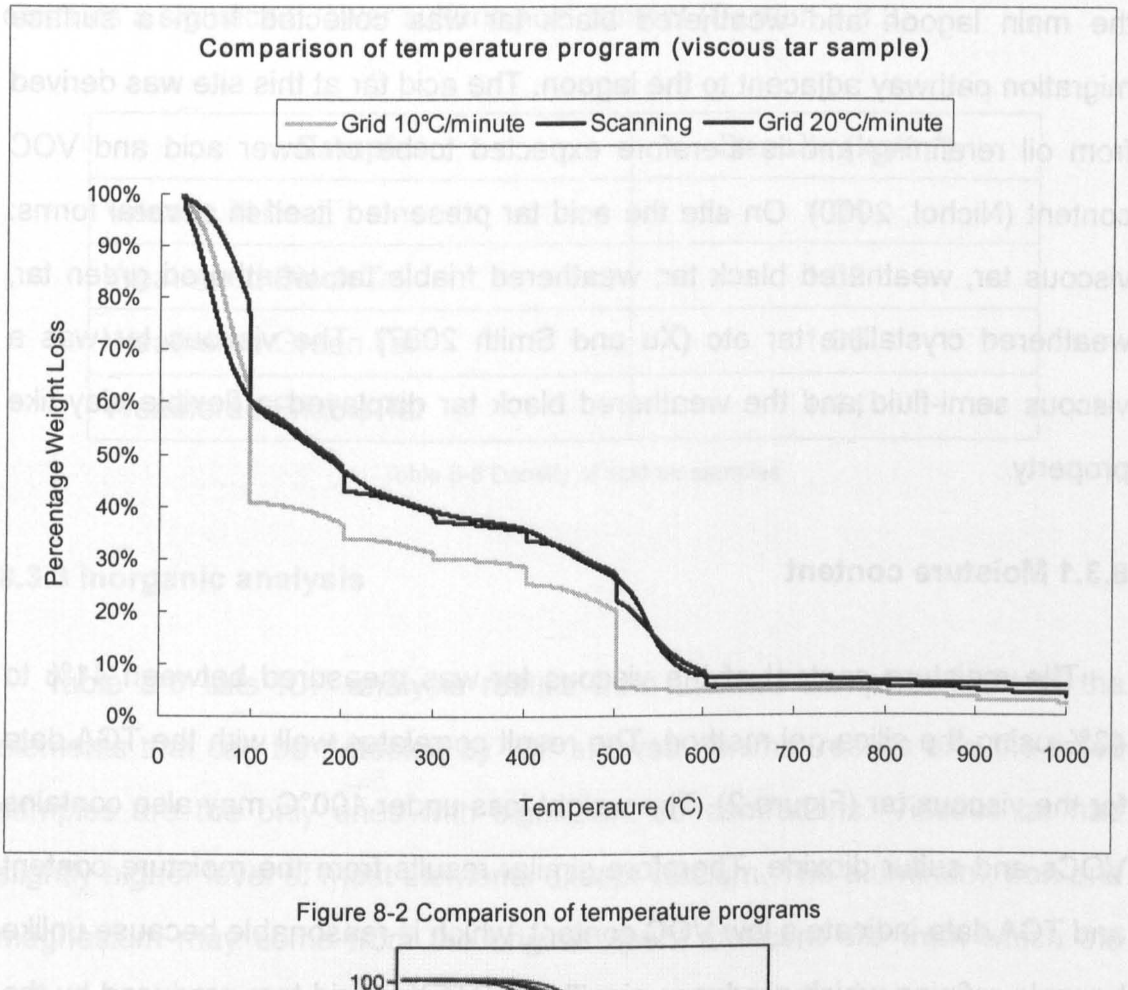


Figure 8-2 Comparison of temperature programs

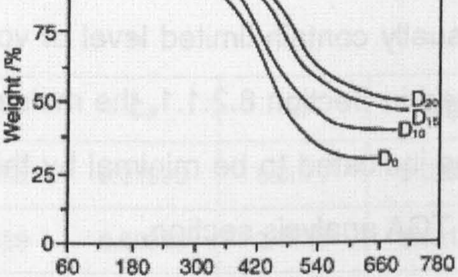


Figure 8-3 TGA scanning curves of coal tar pitches (Lin *et al*, 2004)

8.3 Case Study: Analysis of Viscous and Weathered Black Tar

To provide an illustrative example of data interpretation and cross correlation using the analytical methods discussed, a case study of the analysis of viscous tar and weathered black tar samples from the acid tar lagoon at Hoole Bank, Cheshire (Nichol, 2000) will be provided. Viscous tar was collected at shallow depth (30cm) on a major upwelling location south of the main lagoon and weathered black tar was collected from a surface migration pathway adjacent to the lagoon. The acid tar at this site was derived from oil rerefining and is therefore expected to be of lower acid and VOC content (Nichol, 2000). On site the acid tar presented itself in several forms: viscous tar, weathered black tar, weathered friable tar, weathered green tar, weathered crystalline tar etc (Xu and Smith 2007). The viscous tar was a viscous semi-fluid and the weathered black tar displayed a flexible clay like property.

8.3.1 Moisture content

The moisture content of the viscous tar was measured between 41% to 43% using the silica gel method. The result correlates well with the TGA data for the viscous tar (Figure 2). The weight loss under 100°C may also contains VOCs and sulfur dioxide. Therefore similar results from the moisture content and TGA data indicate a low VOC content, which is reasonable because unlike benzole refining which produces significant BTEXs, acid tars produced by the oil rerefining process usually contain limited level of volatile aromatic organic compounds. As discussed in Section 8.2.1.1, the moisture content of the solid weathered black tar was indicated to be minimal by this method. This will be discussed further in the TGA analysis section.

8.3.2 Density

Table 8-5 lists measured densities of viscous and weathered black tar together with that of weathered green tar and weathered friable tar for comparison. The reported density of acid tars is usually between 1140 to 1430 kg/m^3 (Frolov *et al* 1980, Nancarrow *et al* 2001), which is higher than the density measured for current acid tars. It is inferred that this is due to sulfuric acid content – the reported acid tars typically contain up to 50% sulfuric acid (density 1960 kg/m^3 content (Frolov *et al* 1980), whereas the tested sample contains a significant lower sulfuric acid content (Section 8.3.3).

Samples	Density (kg/m^3)
Viscous Tar	1.04
Weathered Black Tar	1.02
Weathered Green Tar	1.06
Weathered Friable Tar	1.14

Table 8-5 Density of acid tar samples

8.3.3 Inorganic analysis

Table 8-6 lists ICP analysis results from the two samples. Most of the elements that can be detected by ICP showed minimal results and the listed samples are the only ones with significant concentrations. Viscous tar had slightly higher level of most elements except calcium. The aluminum, iron and magnesium may come from the original spent lubricant oils from which the acid tars were produced (Milne *et al* 1986).

(mg/g tar sample)	Al	Ca	Fe	Mg	Na	S
Blank	0.03525	0.04995	0.0078	0.00615	0.0408	0.0168
Viscous Tar	2.6589	0.60885	2.4285	2.63115	0.3288	2.83305
Weathered Black Tar	0.61755	1.76655	0.26775	0.03015	0.24645	0.8133

Table 8-6 ICP results for acid tar samples (Carried out by The Sheffield Assay Office)

pH and IC analysis of leachates from batch leaching tests (solid to liquid ratio 1:10) are shown in Table 8-7. The viscous tar has a lower pH than the weathered black tar. It may be seen that sulfate is the only dominant inorganic compound and that the calcium level in the weathered black tar is also slightly higher than in the viscous tar. It is possible that the weathered tar was subject to lime treatment in the past, though there is no clear evidence of this.

If all the sulfur was leached as sulfate then 1g of viscous tar would have a minimum of 27.94mg or ~3% of sulfur, almost 10 times of the ICP results. If all sulfur is in forms of sulfuric acid, the sulfuric acid content would be 85.57mg or ~8.5%. Since not all sulfate would be expected to leach in a 1:10 batch test, use of cascade test data (Xu and Smith, 2007) is preferable. Results from such tests on this tar indicate that approximately 65-70% of sulfate has been lost at 1:10 ratio. The above values may thus be underestimated by ~30% As discussed in Section 8.2.2.3, the sulfur level in the ICP analysis will be underestimated due to the release of sulfur dioxide during sample preparation and the sulfuric acid content is overestimated based on sulfate level.

Samples	***pH***	***Na***	***K***	***Mg***	***Ca***	***F***	***Cl***	***SO_4***
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Viscous Tar	1.64	37.61	38.68	336.56	12.51	7.94	40.43	8381.33
Weathered Black Tar	2.45	86.36	28.98	167.30	219.01	3.35	20.29	2945.41

Table 8-7 IC results (Xu and Smith, 2007)

8.3.4 Organic analysis

Toxic organic compounds screening by Static Headspace GC-FID (model: Perkin Elmer Clarus 500 GC), HPLC (model: Perkin Elmer LC Turbo HPLC Series 200) and GC-MS (model: Varian Saturn 2000) found no BTEX, phenolic organics or PAHs in the samples. This is probably because acid tar was produced by oil rerefining, which processes fewer aromatic hydrocarbons. TPH analysis of the viscous tar showed an average level of 7.6% by weight. TPH analysis of weathered black tar found no TPH (discussed in 8.2.3.2). TOC (measured by Shimadzu TOC-V CSH TOC Analyzer in this research) results of batch leaching results (Solid to Liquid ratio 1:10) are shown in Table 8-8. Viscous tar had 5 times more TOC than weathered black tar, mainly because it is easier for it to break up and form a suspension in water and therefore generated more colloids.

Samples	mg/l
Viscous Tar	2329
Weathered Black Tar	407.15

Table 8-8 TOC results

8.3.5 Thermal Gravimetric Analysis

As stated in section 8.2.4, the TGA data could not give direct compositional information for acid tars. It provides only data on the thermal behavior of acid tars depending on their evaporation and decomposition characteristics. The interpretation of the data is not conclusive and needs to be correlated with results of other tests to infer the composition of acid tars. Figure 8-4 shows TGA curves of viscous tar, weathered black tar, weathered friable tar and weathered green tar analyzed by a Perkin Elmer Pyris 1 TGA. Proposed interpretation of the TGA data is also shown.

The weight loss below 105°C is indicative of moisture content and VOCs. In addition, desulfonation of sulfonic acids will release sulfur dioxide, which mainly takes place below 200°C (Bukharkina *et al*, 1993). The high portion of sulfur containing compounds also influences the thermal behavior of acid tars. As discussed in the sulfur chemistry section (Section 4.1.4), there are various species of organosulfur compounds existing in acid tars, e.g. less oxidized disulfides, alkyl and aryl sulfides, and sulfoxides; and more oxidized sulfoxides, sulfones, sulfonates and sulfates (Geraldine *et al,* 1999). These organosulfur compounds will more easily decompose than aliphatic or aromatic hydrocarbons with a similar structure because the C-S bond is usually weaker than the C-O or C-C bond (Clayden *et al*, 2006). Such a feature will significantly alter the thermal behavior of acid tars if compared with coal tar or bitumen as discussed in Section 4.2, especially in low to medium temperature range.

As a general rule, heavier organics will evaporate at a higher temperature than lighter organics, and aromatic hydrocarbons will evaporate at a higher temperature than aliphatic hydrocarbons with the same number of carbon molecules, e.g. Dodecane ($C_{12}H_{26}$) has an boiling point of 216°C, n-Heptadecane ($C_{17}H_{36}$) 302°C, PAHs (C10-C22) 218°C to 525°C. At temperatures higher than 500°C, petroleum range organics (C5-C35) will either evaporate or decompose and only heavy hydrocarbons or waxes will not be vaporized. Therefore, most of the petroleum range organics will be lost below 500°C. However, one important feature of organic mixtures is that cross linked organic compounds will raise the mixture's boiling point (Md AzharUddin *et al* 1997). As an extremely complex organic mixture, acid tar displays some polymer-like features (Frolov, 1981) including cross-linking, which will raise the boiling point of the mixture. The interpretation of the discussion above is shown as the grey area in Figure 8-5.

At temperatures above 550°C, only heavy organics will remain and the remaining weight at even higher temperature is contributed by the residue inorganic ash. It should be noted that such an interpretation is only a guideline. The temperature ranges proposed are not distinct boundaries, especially for petroleum range hydrocarbons and heavy organics, because of the decomposition, cross linking and the presence of organosulfur compounds.

It can be seen that the viscous tar lost 43% of its weight below 105°C, which closely matches the result of the moisture content analysis and the fact that no BTEX was identified in the head space analysis. The rate of weight loss then reduces between 105°C to 400°C, over which 20% sample is decomposed or evaporated. Another weight loss peak appears at ~560°C, where 90% of the sample has been lost. The curve is flat after 560°C and the final residue is 5% of sample weight, which are inferred to be mainly inorganic ashes.

Weathered black tar has a very different pattern. The weight loss below 105°C is only 7-8%. There is a significant weight loss just over 105°C, which may caused by desulfonation of organic acids. Weight loss between

105-560°C was 43-45% and is less smooth compared to the viscous tar, though shows similar rate changes at ~420°C. The residue at 1000°C is 15%. The TGA curve of weathered green tar is more similar to that of viscous tar than weathered black tar, which may indicate that its mobile organic components are less leached because of its close contact with viscous tar in the acid tar lagoon. The residue of weathered green tar is the lowest of all samples. It is inferred that most of them were leached to the top water. The TGA curve for weathered friable tar has lowest weight loss at the low to medium temperature range, which indicates that most of its organic components are in the heavy range. The shape of the curve is also similar to the TGA curves for coal tar pitches shown in Figure 8-3 and the TGA curve for the flow cell leaching residue shown in Figure 7-11(b) in Chapter 7. Such a similarity is the result of complete weathering discussed in Chapter 6, which all mobile components of acid tars had been leached and only inert heavy organics remain.

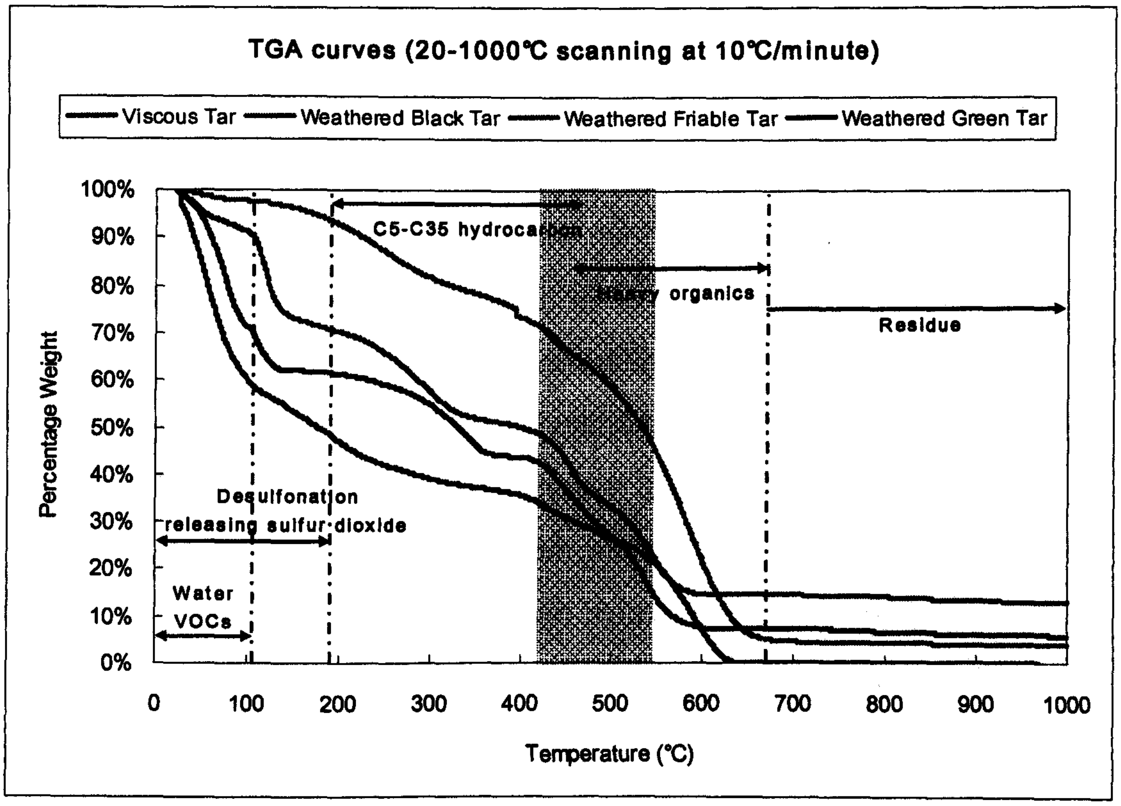


Figure 8-4 TGA curves of acid tar samples

8.4 Data Correlation and Discussion

8.4.1 Data Correlation

The data derived from each test reflects only one aspect of acid tar and may need to be validated by other data. Therefore, data combination and correlation may be performed using information derived from all tests to provide an estimated composition of the acid tar samples and explanations of their different properties. It should be noted that some of the values are estimated from cross-correlation of test data without direct test evidence, such estimation is based on the current understanding of acid tars and may subject to further development of future research.

Based on the data gathered in laboratory tests and the literature, the inferred composition of viscous tar and weathered black tar samples is summarized in Table 8-9. Hypothetical calculated compositions of both samples have also been listed by assuming all moisture content is lost. The total percentage weight without moisture content (55% for viscous tar and 90% for weathered black tar) is normalized to 100% and all other compositional groups are calculated respectively. Viscous tar has greater sulfuric acid content and moisture content than weathered black tar but a lower petroleum range organic content and residue. It is inferred that during the weathering process, the inference that weathered black tar loses some of its acidity and moisture content but retained certain level of organic solvents, which explains its flexible, clay-like property. It is thus postulated that the lower estimation of the petroleum range organics and the upper range for the heavy organics is likely to be correct as these would most closely correlate with the normalized viscous tar data.

Table 8-9 Summery of viscous tar and weathered black tar composition from Hoole Bank

Categories	Viscous Tar	Weathered Black Tar	Viscous Tar (excluding water content)[2]	Weathered Black Tar (excluding water content)[2]
Moisture Content	43% - 45%	7-10%[3]	0%	0%
Sulfuric Acid	3%[1]-12%	0.8-1%[1]	6%	1.1%
Volatile Organics	0%	0%	0%	0%
Petroleum Range Organics (C5-C35)	7-8%	20-50%[4]	14%	22%-55%
Heavy Organics (>C35)	23-40%	27-60%	63%	30-67%
Residue (inorganic ashes)	5%	12%	9%	13%

Note: [1] total sulfuric acid is calculated from the cumulative results of cascade leaching tests data (Xu and Smith 2007) and is calculated by assuming all sulfate correlates to sulfuric acid. Total acidity, including sulfuric acid and organic acids, is not available in forms of percentage weight because organic species are highly variable.

[2] Column 3 and 4 are calculated weight distribution by excluding moisture content.

[3] Estimated using TGA data.

[4] Estimation based on the TGA data, needs to be validated.

This case study has examined acid tars from one single site. Results of this paper are only valid on the sample taken in the studied site and acid tars from other sites may exhibit different behaviors. However, in terms of acid tar characterization, techniques used in this research should be versatile.

8.4.2 Discussion

8.4.2.1 Analytical Techniques

The chosen analytical techniques to be applied to acid tars should depend on the purpose of the study and be on a site-by-site basis. As an easy and economic technique, TGA analysis is recommended as an initial screening technique to provide useful information to guide further investigation. The toxic organic compound screening methods (BTEX, PAHs, phenols) will be required when assessing human health risks of acid tars. Otherwise, group parameters are recommended to reflect the organic contamination, such as TOC for aqueous phase or TPH for solid tar. However, the TPH may not fully reflect the C5-C35 range organic components of acid tars due in part to the sulfonic acid content, which is unlikely to be extracted by hexane because of its high polarity. Physical properties such as density are useful parameters for the study of migration of acid tars.

As one of the major environmental impact of acid tars, the analysis of the emission of sulfur dioxide and other volatiles is necessary. Pensaert (2005) reports a method to determine the sulfur dioxide emission. The test set-up blows a controllable flow of pure air over a known volume (with known exposed surface) of acid tar, and the outlet air is chemically analyzed for any compound of interest.

Further development of analytical techniques for acid tars is required for viscosity measurement and sulfur related parameters (total sulfur content, organic sulfur content, sulfuric acid content) for further understanding of the material.

8.4.2.2 Implication of Environmental Assessment

To assess the environmental impact of acid tars, certain analytical techniques can be applied to measure the relevant parameters.

For emission problems, the method reported by Pensaert (2005) can be applied to determine sulfur dioxide emission and head space analysis can be used to determine volatile organic emissions. For leaching characteristics, pH, IC and TOC will reflect the level of contamination in acid tar leachates. For human health risk assessment, the potential hazardous components of acid tars can be analyzed by ICP and organic toxic compound screening techniques (head space GC-FID, HPLC, GC-MS). These will determine the heavy metal content, BTEX, PAHs and phenols.

The bulk migration ability of acid tar is a more complex scenario, and is primarily determined by its density compared to the capping soil if any and its viscosity that determine the fluidity. The composition of acid tar also influences its migration ability. The heavy organic components of acid tars (C>35) can be regarded as inert and not mobile. The petroleum range organics (C5-C35) are important to the migration ability of acid tar because they mainly act as solvent and keeps acid tar in its semi-liquid form.

8.5 Conclusions

Modified analytical techniques suitable for acid tars have been recommended as follows:

- Water Content: Silica gel absorption method.
- Density: modified British Standard Immersion in water method.
- Inorganic and heavy metals: ICP analysis for initial screening on solid acid tar samples (The method is inappropriate for mercury, lead and in particular sulfur) and IC for leachate analysis.
- Organics: Hazardous organic compound screening using Head space GC-FID analysis for BTEX, GC-MS for 16 PAHs and HPLC for phenols.
- Group parameters: TOC for leachates and TPH for petroleum range organic content.
- TGA analysis on solid acid tar samples for weight distribution estimation and comparison between viscous tar and weathered tars.
- Methods for combining data from different analysis to give a clearer picture of acid tar composition have been outlined.

The above recommendations are a fairly exhaustive list of all potential analytical methods for acid tars and it is not necessary that all these methods have to be applied.

8.6 Appendices - Procedures of analytical methods of acid tars

1. Moisture Content - Silica Gel Absorption
    a) Weigh 500g of silica gel and transferred into a desiccator.
    b) Weigh 5g of acid tar sample in a small glass container, spread the sample evenly to maximize surface area and transferred into the desiccator.
    c) Seal the desiccator for 48 hours or until the sample has dried completely at 25°C.
    d) Weigh dried acid tar sample and discolored silica gel.
    e) Calculate moisture content of the sample using the following equation:

    Moisture content = (weight loss of acid tar + weight increase of silica gel) / 2) * 100%.
2. Density
    a) Prepare a large beaker filled with purified water and place it on a balance. Record the reading.
    b) Transfer a portion of acid tar samples into a weighed 1.5cm glass tube (m_{glass}). Make sure there are no air gaps. Weigh the filled glass tube and get weight of the sample ($m_{tar} = m_{filled\ tube} - m_{glass}$).
    c) Pour liquid wax into the tube to seal the sample. Tilt the glass tube in an angle to avoid trapped air gap when pouring. Weight of wax cover $m_{wax} = m_{waxed\ tube} - m_{filled\ tube}$).
    d) Tie the waxed glass tube with a string and completely immerse it with water. Record the reading when stabilised.
    e) The density of acid tar samples can be calculated using the following equation:

    Density = m_{tar} / (reading$_{after\ immersion}$ – reading$_{before\ immersion}$ – (m_{glass} / density$_{glass}$) – (m_{wax} / density$_{wax}$))
3. ICP Sample Preparation

- g) Weight 10 grams of acid tar samples and transfer into a ceramic plate.
- h) Place the plate in a oven and heated at 720°C for 24 hours.
- i) Add 3ml of concentrated nitric acid (69%) to the plate. Place the plate on a 80°C hotplate for 2 hours to digest.
- j) Transfer the liquid to a 15ml container and add deionized water until 15ml.
- k) A blank sample with same procedure describe above without acid tar is also prepared for comparison.
- l) Send the 15ml sample for ICP-AES analysis.

4. Ion Chromatography Sample Preparation
   - f) The leachates are filtered by a 0.45µm filter paper.
   - g) Depending on the pH and color (an indication of its contamination level) of the leachates, it needs to be diluted for 10 to 50 times respectively.
   - h) Transfer the diluted leachate into IC sample valve and seal it with a filter cap.
   - i) A blank sample with same procedure describe above using deionized water is also prepared for comparison.
   - j) Place the valves into sample rack and feed it to the auto sampler of DIONEX DX 120 IC.
5. TPH
   - m) Weigh 5g of acid tar samples and transfer into a glass container
   - n) Add 20ml of hexane into the container, seal the container and place it in a 80°C water bath for 24 hours.
   - o) Cool the sample for 2 hours. Transfer the extracted liquid to another weighed container.
   - p) Place the extracted liquid into fume cupboard to dry. Weigh the dried container.
   - q) A blank sample with same procedure describe above without acid tar is also prepared for comparison.

r) TPH (hexane extracted hydrocarbons) content is the weight difference between the dried container and clean container.

Chapter 9 Discussion

The preceding chapters have sought to investigate specific aspects of acid tars and related literature. The aim of this chapter is to draw together these findings and discuss the implications for the assessment and remediation of acid tar lagoons.

9.1 Assessment of Acid Tar Lagoons

Due to the heterogeneous nature of acid tars, the assessment of acid tar lagoons should be considered on a site-by-site basis. For each site, an initial desktop study of site history is necessary prior to planning a site visit. The desktop study should pay attention to information that would influence the properties of acid tars and their behaviors on site, e.g. the production process, co-disposed materials and previous treatment/remediation if any. A list of features/evidences that should be looked for during the site visit should be generated.

In the site visit stage, there are a number of features of an acid tar lagoon that should be pay particular attention to: (i) evidence of emission problems, e.g. acidic smells that indicates sulfur dioxide or aromatic smells that indicates volatiles; (ii) different forms of acid tar: weathered black tar and weathered friable tar are usually found on surface migrations indicating bleeding of the tars, weathered green tar may be found under standing water or be indicative of historical standing water. Unless found in active migration pathways, the "fresh" viscous tar is not expected to be found in the surface. (iii) Stability of the lagoon. The migration of acid tars via different pathways is often the evidence of instability of an acid tar lagoon. Sometimes the acid tars seems to be able to migrate in a lava-like pattern in capped sites, which bleed through the capping layer and elevate the migration point into the highest topographical level. (iv)

Contamination of surface water or top water if any. (v) Seasonal factors. Acid tars are more fluid and mobile in the summer than it in the winter.

The sampling of acid tars is often subject to a found-and-collect basis because of the complexity of the site conditions. If there is more machinery available, more sampling techniques, such as trial pitting, cone penetration and boleholes (Chambers, 2001), can be applied to collect more homogenized and representative sample. The samples can be tested depending on the aim of the study.

Based on the desktop study and site visit, the potential contamination linkages can be summarized, which can be used to assess the environmental impact and remediation options of the site.

The current research was limited to surface and shallow depth samples. The conditions of the main tar body were unknown. The simulation of groundwater interaction with acid tars by the flow cell leaching test is based on the assumption that the viscous tar sampled in this research is the "fresh" acid tar. Being in the ground for more than 30 years, the nature of the acid tar could have been changed either naturally, or by mixing with co-disposed materials or surrounding soil. The acid tars that contact with surrounding environment may change its nature and act as a barrier that preventing further leaching of inner tar body. The access of subsurface of acid tar lagoons is therefore, one of the most interesting further research areas.

9.2 Leaching and Chemistry

Although all components of acid tars may be hazardous to human health if contacted directly, there are components which of greater concern because of their greater mobility, either dissolved in or in forms of colloids. Furthermore, the presence of these components makes acid tar itself more mobile and causes the bulk migration problem. As discussed in Chapter 6, these components are sulfuric acid and light to medium range organic compounds

(BTEX, PAHs and other petroleum range aliphatic and aromatic hydrocarbons) which act as solvent to keep acid tar in its semi-liquid form.

Results from batch leaching tests showed the worst case scenario, in which all forms of acid tars that were tested were capable of generating significant level of contamination (low pH, high sulfate and TOC). Cascade tests indicated a capacity for relatively long term leaching. Although sulfate diminished in the later stages, the buffering like behavior caused by organic acids and diffusion keep pH at relative low level and TOC still presented at significant level at the end of the tests. Physical disturbance was raised as an important factor that influences the leaching. Weathered tars had low level of leaching than the viscous tar.

By carrying out flow cell tests, long term leaching behavior of acid tars under limited tar/water interface has been studied. Although fluctuating, the overall level of leaching is much lower than in the equivalent cascade test. The timescale of such a leaching is expected for months in the model soil and could be significantly longer in natural environment. Migration of acid tars, driven by gravity, was the most important feature of flow cell leaching test. The migration accelerated the leaching process and expanded the contamination area. However, the nature of “fresh” acid tar changed during the migration process and reduced the level of leaching by limiting permeability of migrated area and trapping some of mobile contaminants.

Results of leaching tests of acid tars implied that although “fresh” dumped acid tars may be able to leach significant level of contaminants into the environment, the environmental impact of present acid tar lagoons, most has more than 30 years of history, will be minimized if not disturbed. The physical stability problem of acid tar lagoons is often caused by capping or other previous treatment.

Uncertainties still remain, especially within the extreme chemistry of acid tars and the migration characteristic. Unlike a DNAPL which usually contains organic mixture, the sulfuric acid content of acid tars makes the chemical processes within acid tars more complicated. The mechanism that binds water, sulfuric acid, sulfonic compounds and other hydrocarbon into acid tars and its influence of the migration ability of acid tars have not been fully understood.

9.3 Weathering

Weathering is a unique characteristic of acid tars, a number of forms of acid tars had been identified during the site visit, each had different physical properties and leaching behavior. By summarizing information gathered from leaching test and instrumental analysis, a conceptual model of acid tar weathering is proposed in Chapter 6 and further discussed in Chapter 7 and Chapter 8. The compositional difference between these forms of acid tars determined their various properties and environmental behaviors.

9.4 Biology

Despite the fairly extreme environment (low pH, high hydrocarbon concentration) in and around acid tar lagoons, biology, particularly microbial and plant life does not seen to be inhibited by acid tar lagoons. In the acidic top water (pH 2.84) of Hoole Bank, algae has been found in "pond-weed" like colonies, which may create a micro-environment within the colonies that is able to neutralize the acidity and utilize the organics as a carbon source. The weathered green tar found under the top water of the main lagoon may also be influenced by microbiological activities, similar dark green colored coating has also been found in some of the cascade leaching test residues. A number of vegetation species were typically found within the site areas of most acid tar lagoons visited. Most of the vegetation seems to grow healthily closely around the main lagoon and migration pathways. Such observation may suggest that unless directly contacted, there is little evidence of the phytotoxity of the surrounding environment of acid tar lagoons, though the vegetation is typically acid loving.

9.5 Remediation

As discussed in Section 2.4, the remediation of acid tar lagoons falls into two categories: source control and pathway control. Previous remediation practices have mainly focused on source control techniques such as incineration or stabilization. The most common pathway control technique applied was the addition of a capping layer to an exposed lagoon surface to break the contamination pathways. However, such approaches usually led to stability problems and encouraged the migration of acid tars. It is therefore, not a long term and sustainable solution.

A sustainable pathway control approach for the management of an acid tar lagoon should consider the following contamination pathways: (i) gas emission at exposed surfaces; (ii) surface water contamination; (iii) groundwater contamination; (iv) acid tar migration offsite.

For open acid tar lagoons, accumulated top water often acts as a barrier that prevents the emission of sulfur dioxide and volatiles. The top water and surrounding vegetation also forms a natural wetland system: the contaminants contained in the water (acidity, sulfate and light hydrocarbons) may be digested, stabilized or sorbed by the local micro-organisms and vegetation root zones. This could be further exploited as has been done for acid mine drainage.

For capped acid tar lagoons, most of the contamination linkages have already been broken and the major issue is that of stability, e.g. tar bleeding and migration. There are several approaches to solve such a problem, including use of a layer of geotextile between the tars and capping layer or using a light capping material such as flyash. However, concerns remain about pressurization of the tar body and bleeding beyond the geotextile, or accumulation of gas beneath the geotextile. .

In the subsurface and regions that below the water table, the acid tars may be able to form a self-stabilized system which restrain the contaminants within the site because of its low permeability. There may be a transition zone or smear zone through which the tar may migrate and contaminate the soil. However, the transition zone may be regarded as diffusion limited natural barrier which makes the leaching of acid tars into a long term processes. Results of cascade and flow cell tests also indicate such a possibility.

Monitored Natural Attenuation, introduced in Chapter 5, is considered to be a potentially viable option for the environmental management of acid tar lagoons and worthy of further investigation. In the transition zone where the soils are smeared by migrated acid tar, the high level of acidity and organics may limit biological activities. However, once within the main groundwater flow, the acidity, sulfate and TOC concentrations will be lowered by dispersion and diffusion processes. The micro-organisms will be able to handle the plume more efficiently. For acidity and sulfate, the concentration in the flow cell tests is already below or close to the acceptable level (ICRCL 59/83: pH<5 and sulfate <2000 for domestic garden, allotment and landscape area; Flow cell test pH 4.5-5 and sulfate less than 10mg/L). Physical dispersion and dilution will render levels even lower. For organics, Williams *el al* (2001) suggested that the microbial activities are optimized where the concentration of organics is in the range of 60-100mg/L. The flow cell test showed that the TOC level of leachates is 10-50mg/L, which theoretically should be amenable to breakdown by micro-organisms. However, the existing literature of MNA on coal tars or NAPLs usually refers to aliphatic hydrocarbons or aromatic hydrocarbons such as oils, phenols or PAHs, the acidic sulfonic acids components of acid tars may require specific sulfur-reducing micro-organisms to digest them and whether such organisms could exist in symbiosis with other bacteria, or whether they will compete with each other is unknown. Further discussion of these microbiological activities is beyond the scope of this research and should be examined by future research.

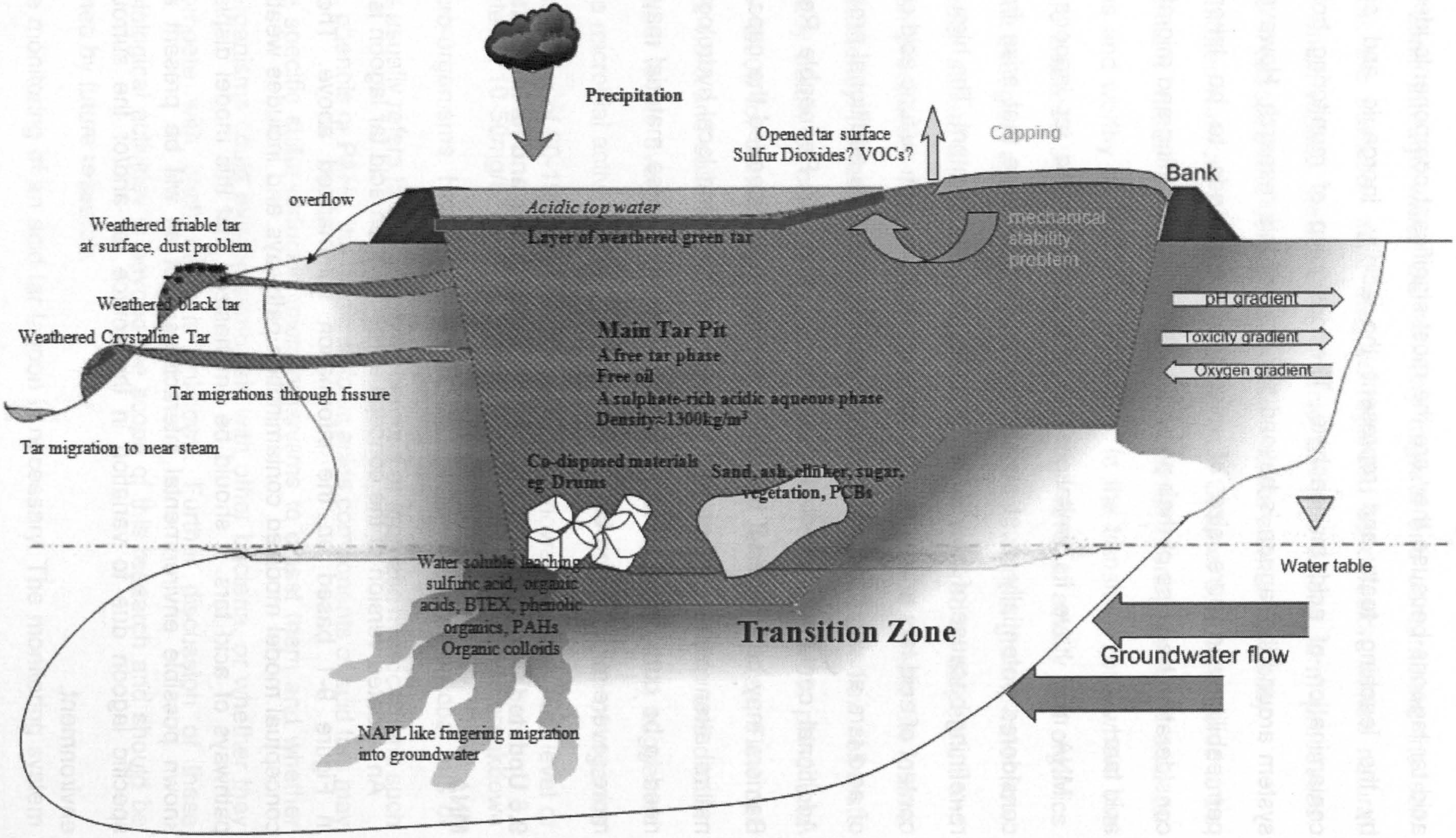
The monitoring of an acid tar lagoon is necessary. The monitoring system needs to be established by choosing appropriate parameters and monitoring locations. pH, sulfate and TOC is recommended as monitoring parameters for acid tar lagoons because they are the most significant components identified by the leaching tests and represent the acidity, inorganic and organic contamination of acid tar leachate. The designing of monitoring bolehole system around the lagoon is beyond the topic of this research. However, the permeability and pore size of underlying soil needs to be taken into consideration because of their potential influence of leaching and migration of acid tars.

MNA may have its limitations when applied to acid tar lagoons. It is considered potentially most suitable for acid tar lagoons that arise from oil re-refining because of their low sulfuric acid and VOC content. The high BTEX content of acid tars arising from benzole refining and high sulfuric acid content of acid tars arising from white oil production may cause additional problems. Additional contamination control techniques, such as Permeable Reactive Barriers may be needed if the contamination level exceeded the capacity of natural attenuation. Furthermore, ground conditions and local hydrology also need to be considered. Acid tar lagoon sitting on coarse material may have more severe migration problems.

9.6 Updated Conceptual Model of Acid Tar Lagoons and Its Implication of MNA

An updated version of the conceptual model of an acid tar lagoon is given in Figure 9-1 based on the information summarized above. The new conceptual model modified contamination pathways and includes weathering pathways of acid tars. It should be emphasized that this model displays all known possible environmental interactions. Not all will be present at any specific lagoon due to variation in the source tar and/or the surrounding environment.

Figure 9-1 Updated Conceptual Model of Acid Tar Lagoon



Compared to the initial conceptual model of acid tar lagoons proposed in Section 5.2, the added/altered features of the updated model are listed below:

a) Weathered green tar under top water

Weathered green tar was discovered during site visits to the Hoole Bank acid tar lagoon under the surface water. Such a form of the weathered acid tar was most likely due to the underwater weathering process of losing volatiles and water soluble components (soluble inorganics, sulfuric acid, sulfonic acids and other organic acids, soluble organosulfur compounds etc) without losing water. Microbiological processes may also contribute to the formation of weathered green tar. The detailed weathering conceptual model is proposed in Section 6.5.1.2.

b) Weathered black tar in the migration path

The most distinct feature of this intermediate weathered form of acid tar is its clay like flexibility. Such a form of weathered acid tar is attributed to a weathering process offset by a supply of water, sulfuric acid and organic solvent by diffusion from fresh viscous tar. The detailed weathering conceptual model is proposed in Section 6.5.1.2.

c) Weathered friable tar on an exposed surface

This final form of weathered tar found at exposed surfaces at a number of acid tar lagoons visited, generates the lowest level of contamination in batch and cascade leaching tests as discussed in Chapter 6. The main problem concerning weathered friable tar is proposed to be its dust form, which might be easily blown offsite by wind.

d) Weathered crystalline tar

This is a form of weathered tar found in the tree shaded area. It is the strongest form of acid tar observed. Its crystalline form may be due to the slow loss of water which may encourage the formation of crystals. The detailed weathering conceptual model is proposed in Section 6.5.1.2.

e) Removed accumulated BTEX & LNAPL

Based on the the analysis data discussed in Chapter 8 and the flow cell leaching data of Chapter 9, the acid tar samples tested did not have significant level of BTEX or LNAPL. The feature is therefore removed in the updated model. It should be noted that this did not eliminate the possibility of the accumulation of BTEX or LNAPL in other acid tar lagoons.

f) Water soluble leaching

The water soluble leaching feature is updated based on the data from leaching test and acid tar analysis. The organic colloids discussed in Chapter 6 are also a major source of aqueous contamination of acid tars.

g) NAPL like fingering migration into groundwater

The NAPL like fingering feature of acid tars introduced in Section 4.3 and further discussed in the flow cell leaching of acid tars replaces the tar migration into ground water feature in the original model. The fingering of acid tar has similar aspects to the NAPL fingering while the most significant difference is the lack of distinct tar (or NAPL)/water interface commonly found in NAPL fingering. Such difference is due to the sulfuric acid, sulfonic acids and other soluble organosulfur compounds in acid tars which render the acid tars hydrophilic, as discussed in Section 7.4.3.

The conceptual model of acid tar lagoon provides a valuable tool to evaluate the feasibility of MNA on acid tars. Natural attenuation processes will happen mainly in the surface water, transition zone and further expanded subsurface area along the groundwater flow.

In the acidic top water, the contamination can be diluted by precipitation, digested by microbiological activities, e.g. pond weed like algae discussed in Chapter 3, and carried away by overflow.

In the transition zone, acid tar will migrate into soil and smear an area of surrounding environment. The processes involved are mainly physical convection of acid tars and chemical sorption of acid tars to the soil particles, as discussed in Section 5.1. In the area more distant from the main lagoon, the level of contamination will lower, and microbial activity will become more active and able to decompose organics. In the groundwater, dissolution, dispersion and diffusion will further lower the concentration of contaminants in the aqueous phase. Therefore, chemical processes and microbiological activities will be able to reduce the contamination to acceptable levels. Therefore, MNA is considered as a potential feasible option for acid tar lagoons which are physically stable.

Chapter 10Conclusions and Further Research

10.1 Conclusions

According to the knowledge gained from the literature, site visits and laboratory tests, conclusions of this research are summarized as follow:

- The components of acid tars that are of high environmental concern are: sulfuric acid,organic acids, sulfate, sulfur dioxide, light and medium range hydrocarbons (BTEX, PAHs and other C5-C35 range hydrocarbons) that are mobile in aqueous either dissolvable or in forms of colloids. Since acid tars are highly heterogeneous materials, these hazardous contaminants need to be identified on site-by-site basis.
- Acid tars may weather into different forms possessing different properties depending on the ambient environmental conditions. Weathering pathways have been postulated in Chapter 6
- Batch leaching tests demonstrated that all forms of acid tar are capable of releasing significant level of contaminants (pH, sulfate and TOC) into aqueous phase under agitated conditions.
- Cascade leaching tests of all tar types up to cumulative solid liquid ratios of 1:60 indicated continued production of significant quantities of TOC, while levels of sulphate stabilized at this point. The pH of acid tar leachate shows a buffering like behavior attributed to the large range of organic acids present in the tar and equilibrium processes occurring at the solid tar/water interface.
- Flow cell leaching tests indicate that the leaching of acid tar in a simulated groundwater flow is a low level, long term process. Acid tar is capable of migrating through voids of a model soil driven by gravity. The timescale of such a leaching is expected to be months for model soil and may be centuries in the natural environment.

- Modified analytical techniques for acid tar analysis are recommended in Chapter 8 and methods for combining data from different analysis to give a clearer picture of acid tar composition have been outlined.
- An updated conceptual model of acid tar lagoon processes has been developed in Chapter 9.
- MNA is considered to be a potentially viable option for the environmental management of some acid tar lagoons and is worthy of further investigation. The nature of the acid tars and conditions of the natural environment need to be considered when assessing the feasibility of MNA.

10.2 Further Research

With almost no preceding research to build on, this research project has by its very nature been a foray into largely unknown territory. Thus many interesting issues have been raised and some of the conclusions made in this research need to be further validated. Key issues for further research are listed as follows:

10.2.1 Weathering

The conceptual model for the weathering of acid tars requires further validation. The laboratory weathering test in this research only achieved weathering from viscous tar to weathered friable tar. The weathering mechanism of weathered green tar and weathered crystalline tar, need to be validated by further research. The key factors that influence the weathering of acid tars are identified as moisture and organic solvent content by this research. However, these parameters are limited to acid tar itself. There may be additional natural conditions that influence the weathering process, which need to be further studied. The formation of weathered crystalline tar is of interest because of the generation of crystals and its extraordinary hardness. Compared to the wind blow problem of weathered friable tar and bulk migration ability of weathered black tar, weathered crystalline tar is considered to be the most stabilized form of acid tar. Further study of the weathering process may lead to the development of potential remediation options.

10.2.2 Migration and Leaching

Migration of acid tars is another key environmental behavior of acid tars that requires further study. This refers to surface migration and migration into groundwater. At the surface, the migration ability of acid tars is mainly dependent on the tar viscosity, which was not studied in this research. The analytical methods of measuring viscosity of acid tars need to be developed, as proposed in Chapter 8. The temperature dependence of viscosity, as well as tar composition (moisture, sulfuric acid and organic solvent content) need to be studied. The migration ability of acid tars through a small fissure is also of interest. In groundwater, the migration ability of acid tars is mainly determined by its interaction with water. Flow cell tests showed that viscous acid tar can be partially dissolved in the water which enhances its migration ability under saturated conditions. The migration was staged and the migrated area was able to trap some water soluble contaminants. The mechanism of such a behavior has not been fully understood. Further flow cell leaching tests using different model soils and under various conditions (water flow rate, temperatures etc) need to be carried out to further elucidate the phenomena.

10.2.3 Chemical Analysis of Acid Tars

In terms of the chemical analysis of acid tars, some techniques need to be developed. Total sulfur content cannot be accurately measured by this research with the problem of sulfur dioxide vapor escaped during sample preparation for ICP-AES analysis. The acidity of acid tars in forms of sulfuric acid and sulfonic acid (with trace level of carboxylic acids) is difficult to measure separately, while the concentration of sulfonic acids in acid tar samples is of high interest because they are one of the most important organic solvents of acid tars.

10.2.4 Microbiology

Microbiological activities in and around the acid tar lagoons, are important environmental factors of acid tar lagoons. Pond weed like substance, further identified as algae, had been found in the top water of the uncapped study site. Such acid resistant micro-organisms and the micro-ecosystem in the lagoon top water as well as in the ground water, is potentially highly relevant to a natural attenuation system that can prevent contamination proliferation. The study of local species of micro-organisms may lead to bioremediation techniques applicable to acid tars as well as other acidic environments.

10.2.5 Remediation

Many existing remediation techniques may be potentially viable in dealing with acid tar lagoons. They may be further developed by examining the feasibility of existing remediation techniques based on the knowledge studied by this research with adequate modification if necessary. There are also many other potential developments of remediation options, such as the utilization of acid tars. The acid tars may be used as an energy source; the high organic carbon content may be used to produce other valuable products etc.

The scope of this research was to provide a generic understanding of acid tars, their environmental impacts and environmental behaviors. Knowledge gained from this research can be used as a background which leads to further development of all aspects of acid tar lagoons. Due to the limitation of time and resources, such a knowledge base is not perfect. The gaps could be filled by further research suggested above in all related disciplines.

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Appendix

Appendix I Data of ICP analysis

Sample ID	Analyte Name	Ag 328.068	Ag 338.289	Al 167.022	Al 308.215	Al 309.271	Al 396.153	As 188.979	As 193.696	B 249.677	B 249.772
	Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Blank		0.0000	0.0406	0.9817	2.3523	2.0367	2.3967	-0.0292	0.0209	-0.0084	0.0038
Viscous Tar 1		0.0056	0.0601	35.7844	114.1220	109.3956	113.9558	0.0537	-0.0554	-0.0443	0.1239
Viscous Tar 2		0.0211	0.0773	25.9068	116.3359	111.3229	115.8635	-0.0833	-0.0365	-0.0505	0.1339
Viscous Tar 3		-0.0125	0.0444	27.1889	122.2250	117.0590	121.7336	-0.0390	-0.0884	-0.0532	0.1377
Weathered Green Tar		-0.0156	0.0473	37.7023	94.9035	90.8821	94.4852	-0.0745	-0.0261	-0.0656	0.1856
Weathered Green Tar		-0.0157	0.0437	28.4070	85.7524	82.0142	85.4660	-0.0959	0.1110	-0.0496	0.1532
Weathered Green Tar		-0.0169	0.0414	17.2569	72.6104	69.4726	72.3439	-0.1414	-0.0338	-0.0528	0.1575
Weathered Frialble Tar		-0.0146	0.0528	58.7677	224.1649	214.3451	222.7466	-0.0534	-0.1190	-0.0739	0.2021
Weathered Frialble Tar		0.0684	0.1309	35.1145	156.9525	150.2071	156.0013	-0.1052	-0.0615	-0.0611	0.1816
Weathered Frialble Tar		-0.0217	0.0408	34.0393	194.5418	186.2553	194.0689	-0.0180	-0.0820	-0.0605	0.1765
Viscous Tar 2		-0.0569	0.0337	51.1776	213.8543	205.0597	213.7434	-0.0347	-0.2561	-0.1306	0.4031
Viscous Tar 3		-0.0353	0.0361	41.2891	183.3329	175.6589	182.4333	-0.1084	-0.0973	-0.0720	0.2582
Viscous Tar 4		0.0147	0.0803	49.2101	134.5962	129.0289	134.0804	-0.0429	-0.1172	-0.0578	0.2121
Odorous Viscous Tar		-0.0308	0.0374	40.1819	126.1687	120.9769	125.5067	-0.0677	-0.0562	-0.0617	0.2159
Odorous Viscous Tar		-0.0357	0.0379	20.5422	72.6488	69.8569	72.2154	-0.0717	-0.1118	-0.0908	0.2671
Odorous Viscous Tar		-0.0241	0.0435	20.6739	74.5589	71.7092	74.1112	-0.0933	-0.1452	-0.0752	0.2282
Weathered Black Tar		-0.0063	0.0397	9.7677	28.3097	26.8392	28.1080	0.6150	0.6761	0.0325	0.0766
Weathered Black Tar		-0.0064	0.0419	13.3139	46.0899	43.9041	45.9013	0.6546	0.8915	0.0295	0.0898
Weathered Black Tar		0.0321	0.0775	9.9987	49.1037	46.7219	48.9191	0.8830	1.1127	0.0459	0.0991

Sample ID	**Analyte Name**	**Ba 455.403**	**Ba 493.408**	**Be 234.861**	**Be 313.042**	**Be 313.107**	**Ca 227.546**	**Ca 315.887**	**Ca 317.933**	**Ca 422.673**	**Cd 214.440**
	Units	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
Blank		0.0415	0.0423	9.8607	-203.0127	-1756.3415	2.9046	1.4590	1.7213	3.3278	0.0008
Viscous Tar 1		0.1590	0.1570	108.0131	-84.6413	-706.0976	36.3311	17.1465	19.5203	38.1820	0.0021
Viscous Tar 2		0.1556	0.1537	113.4371	-74.6614	-727.6914	41.4435	19.4111	22.0163	44.0826	0.0051
Viscous Tar 3		0.8698	0.8585	117.3961	-59.5197	-576.3303	42.4930	20.4059	23.0696	45.1722	0.0046
Weathered Green Tar		0.3935	0.3868	145.3812	-100.7998	-1027.1516	88.2521	41.5799	46.8374	91.9834	0.0073
Weathered Green Tar		0.7213	0.7108	120.4490	-111.4059	-1015.3832	162.9256	78.3420	88.0562	169.0867	0.0050
Weathered Green Tar		0.3433	0.3376	121.7073	-125.3039	-1267.0406	88.7975	40.9392	46.2860	91.0722	0.0081
Weathered Frialble Tar		0.4269	0.4204	177.9890	23.6045	-56.9722	57.9962	27.5309	30.9609	60.5687	0.0060
Weathered Frialble Tar		0.2689	0.2662	145.1207	-44.7954	-765.1721	59.0476	27.9335	31.4846	61.3000	0.0066
Weathered Frialble Tar		0.9978	0.9801	149.4372	-25.6630	-330.7825	48.9969	22.9339	25.9837	51.6514	0.0049
Viscous Tar 2		0.0240	0.0246	309.2750	27.7689	385.1414	31.0166	15.4627	17.4570	32.4084	0.0199
Viscous Tar 3		0.1291	0.1278	207.1265	36.3412	285.8800	43.0907	20.5709	23.2392	45.5958	0.0103
Viscous Tar 4		0.1751	0.1727	165.9838	-39.5785	-298.1759	42.3184	19.2951	21.7406	43.7768	0.0095
Odorous Viscous Tar		0.2310	0.2272	164.6643	-47.9323	-538.4105	51.6366	24.1954	27.3014	54.1805	0.0079
Odorous Viscous Tar		0.0310	0.0316	195.2906	-90.7779	-1104.9935	41.0763	19.4032	22.0139	42.1454	0.0148
Odorous Viscous Tar		0.0349	0.0354	166.8302	-100.1362	-1071.4957	43.2082	20.5100	23.1581	45.1310	0.0137
Weathered Black Tar		7.5942	7.3465	37.9677	-79.7411	-886.2304	86.0184	41.2908	46.6123	89.5871	0.0203
Weathered Black Tar		7.0171	6.9069	44.5947	-77.8297	-893.6857	122.5649	58.3760	65.6131	128.5568	0.0207
Weathered Black Tar		7.7628	7.6476	48.6239	-51.8065	-525.0575	128.1979	61.3745	68.6996	135.1555	0.0227

Sample ID	Analyte Name	Cd 226.502	Cd 228.802	Co 228.616	Co 238.892	Cr 205.560	Cr 267.716	Cu 324.752	Cu 327.393	Fe 238.204	Fe 273.955
	Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Blank		0.0003	-0.0026	-0.0065	0.0053	0.0012	0.0027	0.1888	0.1574	0.5229	0.6114
Viscous Tar 1		0.0014	-0.0019	0.0129	0.2349	0.1046	0.1087	0.2193	0.1792	68.4998	68.7681
Viscous Tar 2		0.0021	-0.0030	0.0141	0.2562	0.1056	0.1092	0.2399	0.1979	75.5845	75.6718
Viscous Tar 3		0.0044	-0.0009	0.0174	0.2595	0.1159	0.1229	0.2824	0.2405	75.3818	75.5219
Weathered Green Tar		0.0035	-0.0026	0.0147	0.3489	0.0438	0.0533	0.3927	0.3516	104.8256	105.6756
Weathered Green Tar		0.0033	-0.0007	0.0101	0.2854	0.0316	0.0489	0.3919	0.3438	85.2424	85.6154
Weathered Green Tar		0.0032	-0.0011	0.0098	0.2909	0.0320	0.0420	0.5072	0.4663	88.2908	88.7651
Weathered Frialble Tar		0.0025	-0.0029	0.0271	0.3996	0.1883	0.1956	0.3933	0.3424	117.3476	118.9255
Weathered Frialble Tar		0.0041	-0.0009	0.0205	0.3496	0.1318	0.1358	0.3668	0.3227	101.7431	102.8192
Weathered Frialble Tar		0.0023	-0.0024	0.0227	0.3317	0.1707	0.1721	0.4462	0.4120	98.5894	98.3265
Viscous Tar 2		0.0065	-0.0048	0.0249	0.7427	0.1666	0.1655	0.1559	0.0978	230.0018	235.5747
Viscous Tar 3		0.0049	-0.0034	0.0372	0.4729	0.1786	0.1864	0.3079	0.2567	142.3899	142.3421
Viscous Tar 4		0.0042	-0.0039	0.0254	0.3908	0.1417	0.1442	0.2707	0.2240	113.3077	114.1710
Odorous Viscous Tar		0.0045	-0.0025	0.0285	0.4057	0.1348	0.1413	0.2843	0.2363	117.9213	119.0683
Odorous Viscous Tar		0.0059	-0.0033	0.0110	0.4948	0.0781	0.0853	0.1576	0.1062	152.3192	154.4706
Odorous Viscous Tar		0.0054	-0.0033	0.0086	0.4153	0.0714	0.0762	0.1465	0.0981	128.3486	129.7536
Weathered Black Tar		0.0280	0.0426	0.0077	0.0582	0.0077	0.0282	2.6436	2.6216	14.5248	14.5253
Weathered Black Tar		0.0275	0.0453	0.0108	0.0896	0.0105	0.0370	2.4753	2.4546	21.2659	21.2421
Weathered Black Tar		0.0307	0.0539	0.0145	0.0840	0.0084	0.0366	3.2935	3.2758	17.7542	17.5380

Sample ID	Analyte Name	Hg 194.168	Hg 253.652	K 404.721	K 766.490	La 379.478	La 408.672	Li 610.362	Li 670.784	Mg 279.077	Mg 280.271
	Units	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
Blank		0.0170	-0.1644	-64.3704	-0.1460	-5.7989	15.1597	0.4359	0.0013	0.4126	0.4593
Viscous Tar 1		-0.0042	0.3979	-53.8052	10.7038	-37.1981	34.6560	0.4387	0.0165	88.8966	93.6533
Viscous Tar 2		-0.0021	0.4407	-64.4843	11.6893	-37.0747	37.6809	0.4338	0.0194	97.5348	98.2990
Viscous Tar 3		0.0663	0.5483	-64.1679	11.6926	-38.9165	37.1614	0.4327	0.0185	97.7806	103.0589
Weathered Green Tar		-0.0132	0.8598	-45.2851	28.5343	-31.9180	56.9254	0.4659	0.0619	84.8761	85.0969
Weathered Green Tar		0.0205	0.6084	-41.0590	25.3746	22.1511	67.0903	0.4572	0.0462	79.8096	79.4038
Weathered Green Tar		0.0043	0.6566	-39.4106	29.7788	-14.4176	56.5382	0.4676	0.0564	75.0041	73.8834
Weathered Frialble Tar		-0.0090	0.8080	-59.8120	12.0033	-54.0051	56.4833	0.4275	0.0157	148.0780	145.1484
Weathered Frialble Tar		-0.0040	0.6872	-49.4350	12.0495	-40.2258	54.6637	0.4309	0.0144	124.2935	122.2524
Weathered Frialble Tar		0.0133	0.6500	-69.4027	10.3319	-46.5194	49.3106	0.4278	0.0123	123.3155	122.6300
Viscous Tar 2		0.0232	2.0965	-68.3404	27.6234	-164.2374	64.1536	0.4377	0.0505	174.1792	0.0000
Viscous Tar 3		0.0001	1.0148	-27.8841	46.4118	-90.4665	46.3234	0.4621	0.0628	196.3874	0.0000
Viscous Tar 4		0.0148	0.6743	-46.6852	36.8521	-70.0446	41.3596	0.4582	0.0505	155.6731	158.1154
Odorous Viscous Tar		0.0145	0.7493	-38.1690	41.2396	-65.9010	44.6019	0.4622	0.0548	163.3195	158.6064
Odorous Viscous Tar		0.0062	1.2294	-40.5892	36.9000	-76.0687	76.6411	0.4533	0.0492	166.2818	0.0000
Odorous Viscous Tar		0.0179	0.9523	-17.8000	37.6477	-54.8018	78.0454	0.4550	0.0523	172.1753	165.5122
Weathered Black Tar		0.0276	0.0042	-52.0836	7.7398	54.1270	61.7747	0.4388	0.0109	1.6592	1.7905
Weathered Black Tar		0.0014	0.0862	-59.2067	8.5863	66.2295	65.1781	0.4395	0.0109	1.8603	1.9560
Weathered Black Tar		-0.0137	0.0436	-57.4232	9.5207	74.4061	69.4442	0.4448	0.0173	2.5213	2.6581

Sample ID	Analyte Name	Mg 285.213	Mn 257.610	Mn 259.372	Mo 202.031	Mo 203.845	Mo 204.597	Mo 281.616	Na 330.237	Na 588.995	Na 589.592
	Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Blank		0.5033	0.0071	0.0091	-0.0016	-0.0721	-0.0801	-0.0082	4.2446	0.7586	2.7159
Viscous Tar 1		104.8968	1.3706	1.3698	0.3213	0.2807	0.3170	1.0978	8.0996	5.3035	7.2528
Viscous Tar 2		110.4629	1.4485	1.4495	0.1680	0.1181	0.1363	0.9338	7.4817	4.8722	6.7953
Viscous Tar 3		114.7424	1.5222	1.5151	0.0968	0.0759	0.1199	0.9322	7.9285	5.5856	7.5130
Weathered Green Tar		95.3147	3.6761	3.5809	0.0604	-0.0187	0.0775	0.6655	55.4598	60.8465	62.5955
Weathered Green Tar		87.9188	3.3895	3.2956	0.0585	-0.0540	0.0039	0.5853	52.0412	55.7672	59.3616
Weathered Green Tar		81.2890	3.0765	2.9995	0.0477	-0.0624	0.0198	0.4795	49.6671	52.8842	54.2593
Weathered Frialble Tar		160.1570	2.2496	2.2428	0.0435	-0.0361	-0.0116	1.4978	7.0301	5.1364	7.0900
Weathered Frialble Tar		134.5356	1.9976	1.9892	0.0001	-0.1108	-0.0130	1.0104	7.5320	5.5047	7.4445
Weathered Frialble Tar		138.6665	1.8701	1.8676	0.0351	-0.0234	0.0775	1.3353	7.2726	4.9154	6.8402
Viscous Tar 2		189.7729	2.8256	2.9113	-0.0614	-0.0589	-0.0298	1.3536	19.1035	19.6192	21.4820
Viscous Tar 3		208.5261	2.6545	2.6486	-0.0186	-0.0909	-0.0061	1.1632	21.9468	22.3040	24.1691
Viscous Tar 4		174.9673	2.1814	2.1804	-0.0165	-0.0544	-0.0327	0.8683	19.4550	18.2237	20.1220
Odorous Viscous Tar		177.9744	2.2604	2.2518	-0.0135	-0.1030	-0.0464	0.7939	20.2812	20.0494	21.9422
Odorous Viscous Tar		178.3919	2.2274	2.2536	-0.0596	-0.1171	-0.0885	0.3873	18.7011	18.6384	20.5506
Odorous Viscous Tar		183.0350	2.1138	2.1205	-0.1164	-0.1450	-0.1652	0.3397	18.5056	19.0618	20.9349
Weathered Black Tar		1.9275	0.3831	0.3794	0.1140	-0.0075	0.0658	0.2607	11.7017	10.1078	12.0267
Weathered Black Tar		2.1186	0.4821	0.4793	0.0943	-0.0328	0.0504	0.3555	16.3723	14.6943	16.5821
Weathered Black Tar		2.8897	0.4868	0.4791	0.1181	-0.0245	0.0374	0.3823	19.1188	18.7854	20.6683

Sample ID	Analyte Name	Ni 221.648	Ni 231.604	P 177.434	P 178.221	P 213.617	P 214.914	Pb 217.000	Pb 220.353	S 180.669	S 181.975
	Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Blank		0.0272	0.0276	0.0887	0.0058	0.0628	0.0459	0.0536	-0.0773	0.9903	1.1239
Viscous Tar 1		0.0591	0.0915	0.3423	-0.1387	0.1713	0.4278	0.5375	0.1211	55.9438	56.3557
Viscous Tar 2		0.1550	0.1666	0.3275	-0.0738	0.2138	0.4445	0.5110	0.1015	64.9320	65.8080
Viscous Tar 3		0.1129	0.1282	0.3722	-0.0413	0.2729	0.5172	0.5768	0.1158	63.9553	64.6939
Weathered Green Tar		0.0763	0.0997	0.5909	-0.0828	0.4130	0.7500	0.6070	0.1170	106.0149	106.9375
Weathered Green Tar		0.1142	0.1281	0.5119	-0.1303	0.4577	0.7305	0.6207	0.1770	132.3303	133.7007
Weathered Green Tar		0.1239	0.1371	0.3215	-0.0768	0.3384	0.6157	0.5598	0.1170	97.0852	98.1806
Weathered Frialble Tar		0.1408	0.1605	0.4094	-0.4915	0.2154	0.6037	0.9062	0.2270	71.1833	71.7268
Weathered Frialble Tar		0.1082	0.1300	0.3255	-0.2275	0.2203	0.4839	0.8239	0.2181	82.9678	83.6608
Weathered Frialble Tar		0.1916	0.2088	0.2572	-0.2434	0.2344	0.5062	0.7973	0.1800	58.6629	59.4050
Viscous Tar 2		0.1123	0.1182	0.6806	-0.1153	0.3739	0.9029	0.8100	0.0819	288.0977	294.5958
Viscous Tar 3		0.1504	0.1621	1.1137	0.3162	0.8458	1.1379	0.8553	0.1695	157.0036	158.7251
Viscous Tar 4		0.1198	0.1328	0.9274	0.3010	0.6508	0.9895	0.6532	0.1196	112.0731	113.2838
Odorous Viscous Tar		0.1254	0.1440	0.9453	0.3031	0.6800	1.0434	0.6384	0.0969	122.7873	124.4312
Odorous Viscous Tar		0.0583	0.0622	0.4025	0.1397	0.2675	0.7144	0.4579	-0.0109	167.1735	169.8701
Odorous Viscous Tar		0.0605	0.0556	0.4147	0.0018	0.2171	0.6236	0.3566	0.0059	176.4203	179.3935
Weathered Black Tar		0.0200	0.0418	0.6611	0.3031	0.6452	0.6646	9.0175	6.3361	40.7153	41.0831
Weathered Black Tar		0.0353	0.0561	0.5956	0.0339	0.5804	0.6963	9.6252	6.7467	57.7807	58.1619
Weathered Black Tar		0.0486	0.0736	0.6434	0.0035	0.7400	0.8381	11.9209	8.3503	63.0100	63.4000

Sample ID	Analyte Name	S 182.563	Sb 206.836	Sb 217.582	Sb 231.146	Se 196.026	Se 203.985	Si 251.611	Si 288.158	Sn 189.927	Sn 235.485
	Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Blank		1.3941	-0.0002	-0.0087	0.0025	-0.1824	0.1323	0.7834	0.8418	0.0581	0.1436
Viscous Tar 1		58.4045	-0.0527	-0.0371	0.0301	1.4102	0.7147	11.1436	11.2907	1.8157	20.9670
Viscous Tar 2		67.4706	0.0021	-0.0329	0.0161	0.0485	0.2449	4.9336	5.0049	0.3703	21.2990
Viscous Tar 3		66.4955	0.0028	-0.0441	0.0330	-0.1786	0.2522	5.2712	5.3071	0.1899	21.8288
Weathered Green Tar		108.7710	-0.0231	-0.0123	0.0153	-0.3468	0.2584	9.3114	9.4081	0.1416	29.0179
Weathered Green Tar		135.9465	-0.0487	-0.0050	0.0099	-0.1244	0.8344	8.4565	8.5721	0.1325	23.1789
Weathered Green Tar		100.1591	-0.0447	-0.0336	0.0099	-0.1905	0.3915	5.4437	5.4501	0.1116	24.2340
Weathered Frialble Tar		73.4062	-0.0121	-0.0521	0.0409	-0.3605	0.1801	6.0897	6.2213	0.0986	32.4009
Weathered Frialble Tar		85.5736	-0.0634	-0.0095	0.0301	-0.4652	0.1214	6.4784	6.5902	0.0717	28.2242
Weathered Frialble Tar		60.6199	-0.0443	-0.0399	0.0320	-0.3072	0.0963	4.3359	4.4757	0.0968	27.4381
Viscous Tar 2		301.2405	-0.0501	-0.1011	0.0306	-0.7537	-0.4493	1.2338	1.3025	0.0578	62.4067
Viscous Tar 3		162.4219	-0.0263	-0.0435	0.0426	-0.4831	-0.1677	4.4783	4.6266	0.0555	38.7748
Viscous Tar 4		115.3694	-0.0148	-0.0620	0.0335	-0.5634	-0.0918	5.0048	5.0411	0.0630	31.4579
Odorous Viscous Tar		127.1239	-0.0287	-0.0524	0.0334	-0.4225	-0.1077	5.7160	5.7624	0.0675	32.6540
Odorous Viscous Tar		174.1805	-0.0356	-0.0533	0.0193	-0.4816	-0.1118	1.2562	1.3214	0.0419	41.9826
Odorous Viscous Tar		183.3705	-0.0710	-0.0532	0.0159	-0.5899	-0.0508	0.4465	0.4909	-0.0041	35.2286
Weathered Black Tar		41.8267	0.0190	0.0352	0.0155	-0.0828	0.6629	8.6878	8.8517	0.1321	4.0663
Weathered Black Tar		59.1749	0.0195	0.0375	0.0185	-0.1354	0.8618	10.7421	10.9063	0.1218	5.8661
Weathered Black Tar		64.7144	0.0302	0.0446	0.0239	-0.0609	0.7553	10.5261	10.6539	0.1192	4.7951

Sample ID	Analyte Name	Sn 283.998	Sr 407.771	Sr 421.552	V 290.880	V 292.402	V 310.230	Zn 202.548	Zn 206.200	Zn 213.857
	Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Blank		0.1239	0.0065	0.0069	0.0070	0.0020	-0.0959	0.0950	0.0978	0.1595
Viscous Tar 1		1.7036	0.1209	0.1203	0.1130	0.0937	-0.0203	0.4442	0.4420	0.7270
Viscous Tar 2		0.3183	0.1357	0.1413	0.1294	0.1090	-0.0012	0.4614	0.4574	0.7559
Viscous Tar 3		0.1375	0.1411	0.1369	0.1300	0.1096	-0.0002	0.6040	0.6016	0.9848
Weathered Green Tar		0.1464	0.3387	0.3462	0.1198	0.1062	-0.0115	0.3088	0.2924	0.5063
Weathered Green Tar		0.1040	0.4332	0.4367	0.1125	0.0955	-0.0212	0.2505	0.2312	0.4165
Weathered Green Tar		0.0999	0.3310	0.3571	0.1041	0.0924	-0.0224	0.3175	0.3035	0.5170
Weathered Frialble Tar		0.0273	0.2078	0.2158	0.2003	0.1728	0.0638	0.7538	0.7432	1.2249
Weathered Frialble Tar		0.0367	0.2138	0.2219	0.1929	0.1692	0.0667	0.5042	0.4970	0.8154
Weathered Frialble Tar		0.0631	0.2386	0.2488	0.1681	0.1470	0.0294	0.7597	0.7732	1.2719
Viscous Tar 2		0.0406	0.2880	0.3083	0.2455	0.2266	0.0737	0.5613	0.5510	0.9204
Viscous Tar 3		-0.0401	0.2037	0.2165	0.2209	0.1884	0.0705	0.7601	0.7557	1.2314
Viscous Tar 4		0.0050	0.1830	0.1906	0.1813	0.1560	0.0332	0.6006	0.5843	0.9675
Odorous Viscous Tar		-0.0015	0.2053	0.2165	0.1920	0.1675	0.0529	0.5949	0.5873	0.9632
Odorous Viscous Tar		-0.0441	0.3711	0.3900	0.2201	0.1950	0.0806	0.2335	0.2067	0.3641
Odorous Viscous Tar		-0.0669	0.3757	0.3959	0.1741	0.1442	0.0348	0.2492	0.2195	0.3771
Weathered Black Tar		0.1554	0.4967	0.5095	0.1311	0.1250	0.0331	0.7009	0.7168	1.1570
Weathered Black Tar		0.1634	0.5504	0.5630	0.1398	0.1335	0.0396	0.6954	0.7132	1.1603
Weathered Black Tar		0.1663	0.5878	0.6119	0.1416	0.1368	0.0411	0.9294	0.9580	1.5558

Appendix II Data of batch leaching test

Samples	Sample weight (g)	Water (ml)	Temperature (° C)
Viscous Tar A	14.88	148.94	22.1
Viscous Tar B	14.97	150.30	21.1
Odourous viscous Tar A	15.26	152.71	21.2
Odourous Viscous Tar B	15.00	150.22	21.2
Semi-solid Tar A	14.99	149.95	21.0
Semi-solid Tar B	15.50	155.53	22.1
Weathered Friable Tar A	15.20	164.39	24.1
Weathered Friable Tar B	15.41	155.36	22.3
Weathered Green Tar A	15.32	153.65	24.0
Weathered Green Tar B	14.69	147.12	23.3
Weathered Black Tar 1 A	9.00	90.22	24.2
Weathered Black Tar 1 B	14.55	145.61	23.5
Weathered Black Tar 2 A	14.94	149.70	24.4
Weathered Black Tar 2 B	10.67	106.35	23.6
Soil A	15.24	152.28	24.5
Soil B	14.54	147.92	24.2

Samples	pH	TOC	Sodium	Ammonium	Potassium	Magnesium	Calcium	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulphate
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Viscous Tar A	2.25	2329	26.84	<9.00	21.00	146.24	19.54	4.06	32.82	<7.2	<18.00	<15.00	230.17	1422.21
Viscous Tar B	2.32	2469	28.56	<9.00	19.41	150.75	21.39	<3.00	30.81	<7.2	<18.00	<15.00	237.92	1438.89
Odourous viscous Tar A	1.66	3389	37.61	<9.00	38.68	336.56	12.51	7.94	40.43	<7.2	<18.00	<15.00	221.04	8381.33
Odourous Viscous Tar B	1.62	3810	37.76	<9.00	40.58	344.17	13.77	7.30	36.74	<7.2	<18.00	<15.00	225.49	8347.49
Semi-solid Tar A	2.34	2483	24.03	<9.00	13.15	151.09	17.62	3.77	26.00	<7.2	<18.00	<15.00	275.09	1187.66
Semi-solid Tar B	2.4	2163	25.98	<9.00	12.79	148.46	16.64	3.96	27.67	<7.2	<18.00	<15.00	270.93	1191.32
Weathered Friable Tar A	2.4	311.35	21.25	<9.00	<6.00	<6.00	<12.00	<3.00	21.39	<7.2	<18.00	<15.00	262.34	653.01
Weathered Friable Tar B	2.35	291.75	50.76	<9.00	9.08	<6.00	39.27	<3.00	46.16	<7.2	<18.00	18.27	261.70	511.83
Weathered Green Tar A	2.34	267.4	84.25	<9.00	20.47	125.18	109.83	<3.00	19.92	<7.2	<18.00	<15.00	229.04	2869.56
Weathered Green Tar B	2.24	285.3	85.16	<9.00	21.80	128.60	113.47	3.16	18.19	<7.2	<18.00	<15.00	225.95	2818.97
Weathered Black Tar 1 A	2.45	407.15	89.10	<9.00	27.28	173.03	219.94	3.09	22.70	<7.2	<18.00	<15.00	215.52	2916.52
Weathered Black Tar 1 B	2.45	326.15	86.36	<9.00	28.98	167.30	219.01	3.35	20.29	<7.2	<18.00	<15.00	220.01	2945.41
Weathered Black Tar 2 A	3.32	239.9	34.46	<9.00	12.16	84.34	224.26	<3.00	22.63	<7.2	<18.00	<15.00	278.20	1454.46
Weathered Black Tar 2 B	3.27	228.35	32.42	<9.00	11.51	86.99	230.73	<3.00	20.00	<7.2	<18.00	<15.00	274.59	1429.37
Soil A	6.8	32.31	26.85	<9.00	<6.00	8.10	255.24	<3.00	16.96	<7.2	<18.00	<15.00	251.31	599.39
Soil B	6.94	34.5	18.13	<9.00	<6.00	6.30	401.98	<3.00	18.18	<7.2	<18.00	<15.00	252.09	837.76

Appendix III Data of non-agitated cascade test

Sample	Weight (g)
Viscous Tar	10.08
Odorous Viscous Tar	12.38
Weathered Black Tar 1	10.71
Weathered Black Tar 2	12.18
Weathered Green Tar	10.17
Weathered Friable Tar 1	10.00
Weathered Friable Tar 2	10.04
Weathered Friable Tar Site B	10.02
Weathered Black Tar Site B	10.5

Viscous Tar	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	2.13	7218	39.72	6151.68	92.04	3.34	148.08	787.55	28.57
1:10	2.50	1642	14.19	2173.77	29.56	0.39	25.47	136.86	17.90
1:20	3.04	1146	0.88	391.15	12.37	0.22	7.35	49.59	33.26
1:30	3.33	834.8	0.26	106.33	19.72	0.52	2.56	36.03	26.11
1:50	3.53	567	14.10	35.77	29.55	0.94	4.61	32.07	55.74
Odourous Viscous Tar	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	1.75	4897	68.61	8264.34	92.15	3.34	117.75	802.96	2.95
1:10	2.27	1755	21.11	4771.84	27.59	0.62	20.28	188.15	7.38
1:20	2.81	1052	27.38	1760.77	24.24	0.53	11.96	92.56	4.61
1:30	3.15	461.4	0.32	186.46	7.23	0.32	2.45	15.90	28.85
1:50	4.36	259.2	3.60	83.37	3.86	0.65	1.42	10.96	9.00
Weathered Black Tar 1	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	2.59	237.8	15.65	3575.33	128.47	6.02	46.85	299.56	44.01
1:10	2.98	23.49	3.63	674.32	28.73	0.89	10.17	30.93	26.17
1:20	3.21	36.1	2.88	511.48	24.32	0.65	7.73	26.04	24.46
1:30	3.15	42.3	3.09	541.36	20.17	0.55	6.77	32.98	37.01
1:50	3.35	50.9	5.45	351.84	10.99	0.31	2.56	22.89	34.42

Weathered Black Tar 2	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	3.63	316.7	12.63	1209.92	35.79	5.02	18.64	93.72	138.35
1:10	3.72	62.56	0.40	241.33	12.13	0.55	3.53	16.68	29.27
1:20	3.92	49.55	2.90	168.49	9.55	0.39	3.19	12.82	22.86
1:30	3.79	55.11	0.32	186.46	7.23	0.32	2.45	15.90	28.85
1:50	3.71	54.77	4.35	184.08	3.66	0.53	2.07	17.60	40.61
Weathered Green Tar	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	2.48	522.5	0.32	804.74	38.30	1.44	10.31	44.89	4.90
1:10	2.95	138.2	0.00	402.22	16.99	0.52	4.35	20.76	13.07
1:20	3.31	108.9	5.20	257.67	10.28	0.23	2.85	16.32	12.10
1:30	3.42	127.2	3.60	83.37	3.86	0.65	1.42	10.96	9.00
1:50	3.64	123.7							
Weathered Friable Tar 1	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	2.53	432.8	11.80	1397.72	11.82	1.98	15.95	61.63	4.14
1:10	2.99	270.7	0.16	245.08	4.04	0.40	3.93	7.43	0.87
1:20	3.47	480.8	0.00	58.05	4.65	0.14	2.71	5.72	0.81
1:30	3.33	522.5	0.00	30.96	2.00	0.26	2.53	8.34	1.38
1:50	3.30	340.9	7.81	9.56	17.37	0.27	2.43	11.15	10.54

Weathered Friable Tar 2	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	2.43	116	11.80	1640.77	8.19	3.61	6.89	1.55	5.69
1:10	2.95	55.49	3.20	309.68	5.20	0.54	1.56	1.61	2.43
1:20	3.59	61.09	0.00	72.54	4.30	0.13	0.81	3.52	0.72
1:30	3.53	70.01	8.75	42.60	9.80	0.43	2.89	0.07	21.20
1:50	3.50	74.05	4.11	28.77	5.43	0.78	1.31	7.80	6.28

Weathered Friable Tar Site B	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	3.48	38.44	4.66	93.48	2.84	2.67	5.24	1.93	23.16
1:10	4.18	21.32	3.20	18.22	2.39	0.58	2.44	0.23	14.22
1:20	4.52	22.17	0.13	3.87	1.44	0.12	0.49	0.50	16.86
1:30	4.20	25.72	0.15	7.86	1.09	0.11	0.51	0.38	16.20
1:50	4.13	29.7	3.73	7.92	2.02	0.07	0.75	0.40	15.68

Weathered Black Tar Site B	**pH**	**TOC**	**Chloride**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
S:L ratio		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	2.69	332	8.01	1086.65	19.86	4.10	4.72	1.71	82.14
1:10	3.58	162.6	0.23	111.83	3.99	0.34	0.40	0.17	21.25
1:20	3.58	207.1	0.00	95.04	1.43	0.01	0.27	0.17	10.76
1:30	3.43	356.6	2.52	210.51	4.08	0.19	0.57	0.23	9.39
1:50	3.08	361.6	4.65	349.29	4.64	0.36	1.09	0.34	13.26

Appendix IV Data of slow-agitated cascade test

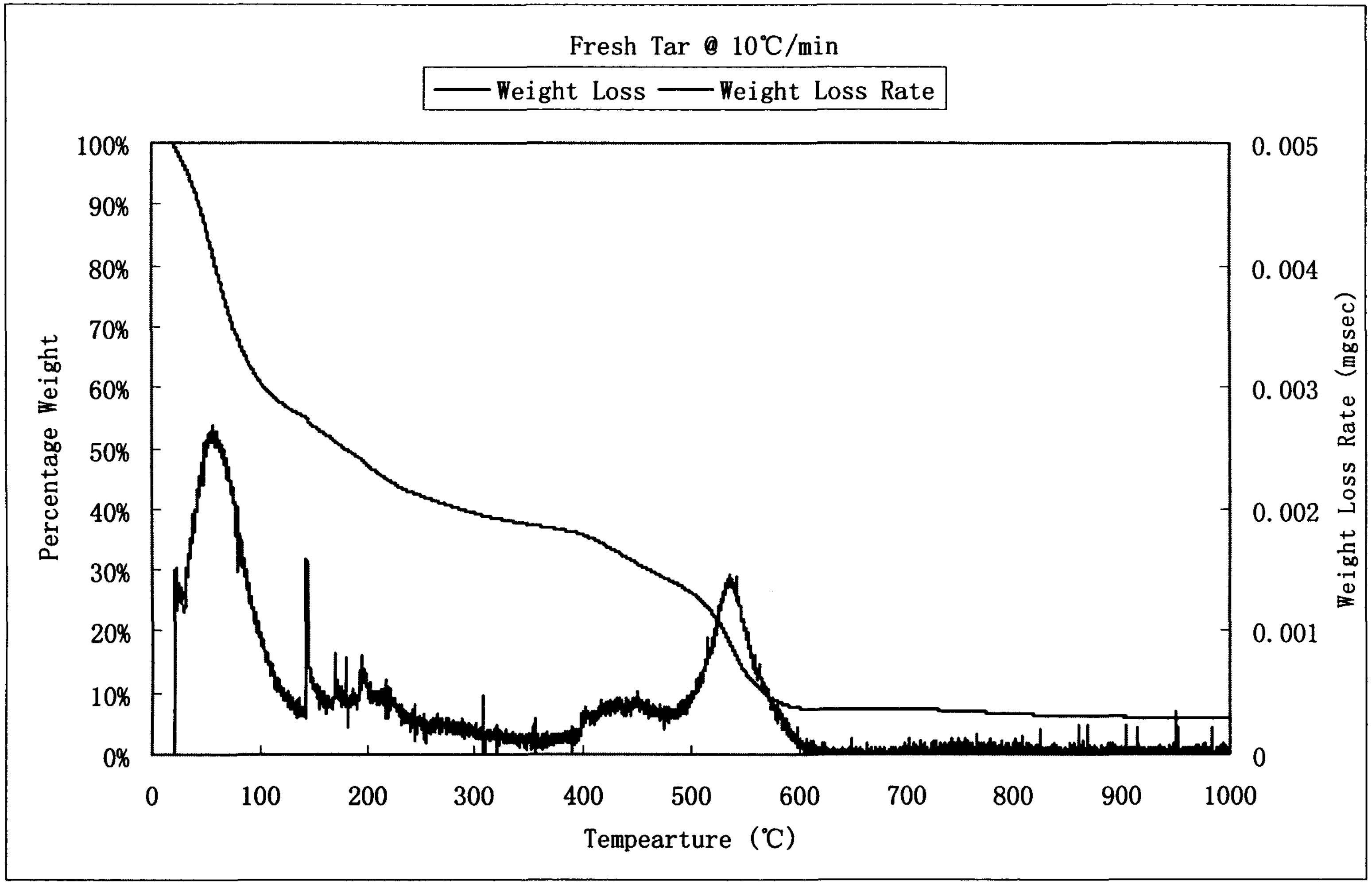
Sample	Weight (g)
Viscous Tar	10.175
Weathered Black Tar	10.796
Weathered Friable Tar	7.451
Weathered Crystalline Tar	10.382
Weathered Green Tar	10.817
Weathered Black Tar Site B	10.532
Weathered Friable Tar Site B	10.504

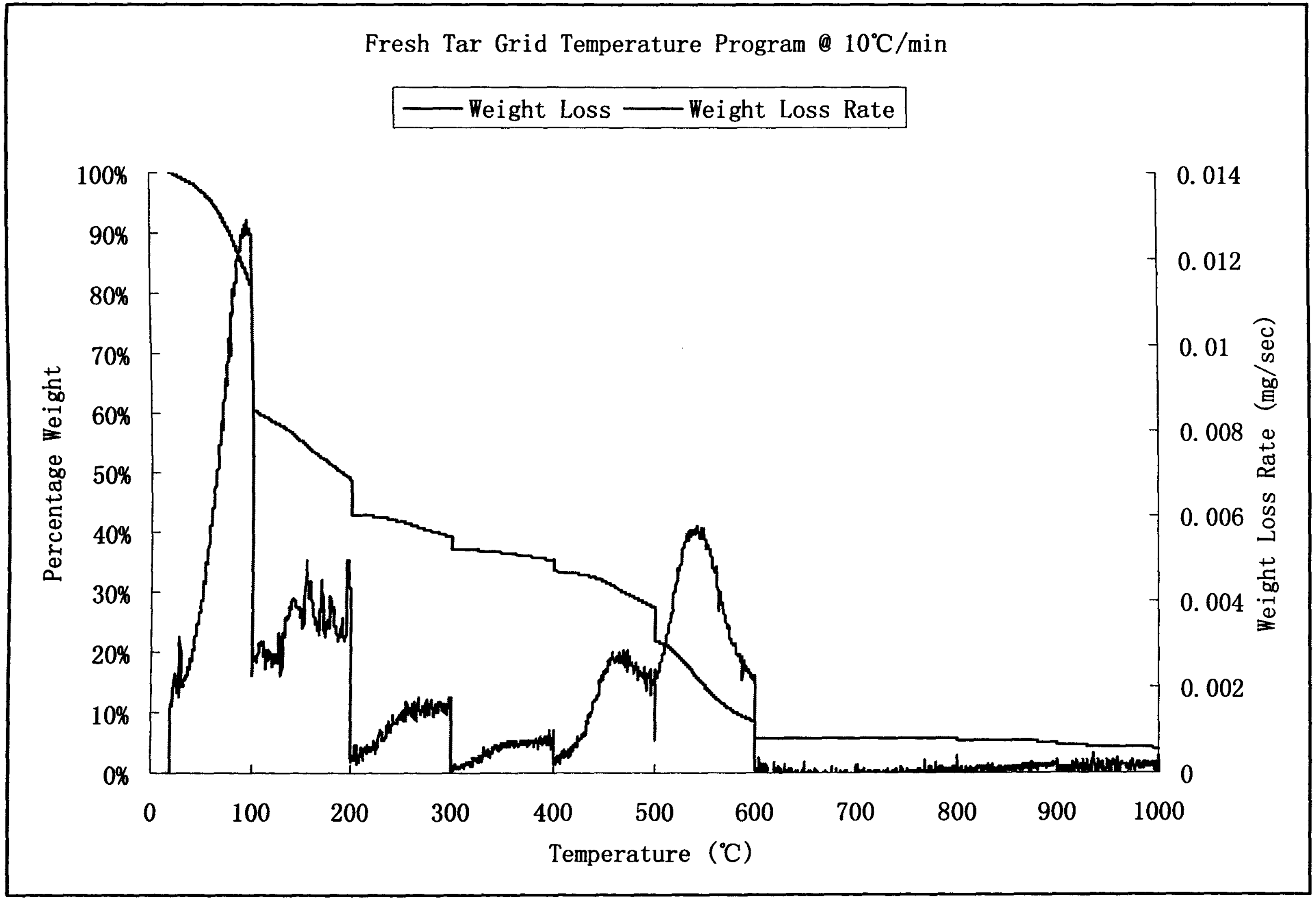
Sample	**Conductivity**	**Turbidity**	**Temperature**	**pH**	**TOC**	**Chloride**	**Nitrate**	**Sulphate**	**Sodium**	**Ammonium**	**Potassium**	**Magnesium**	**Calcium**
Viscous Tar	**µS/m**		**(° C)**		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
1:2	331.3	Over Range	19.4	1.48	3558	23.35	0.00	5002.17	55.65	2.55	67.20	273.15	3.45
1:10	299	Over Range	17.9	2.06	2312.7	23.32	0.00	3829.29	75.42	1.62	60.09	240.03	3.90
1:20	271.4	Over Range	20.3	2.55	1408.2	18.24	2.02	1345.73	13.97	3.69	24.77	120.15	3.53
1:30	245.8	Over Range	19.5	2.98	1074.3	9.70	2.13	426.38	41.28	0.39	15.31	44.33	26.34
1:40	234.6	Over Range	17.5	3.11	630.6	11.02	1.84	210.55	12.55	3.17	10.13	47.03	5.01
1:50	216.2	Over Range	20.5	3.46	396.9	8.86	8.70	69.37	45.14	0.80	10.43	30.37	17.11
1:60	207.7	Over Range	17.2	3.56	357.6	10.14	0.00	43.12	33.37	9.76	6.39	27.53	17.13
Weathered Black Tar													
1:2	180.7	62.6	13.3	3.97	767.4	17.46	6.22	2674.24	83.25	5.10	44.70	179.85	173.55
1:10	181.4	5.7	17.2	3.98	202.98	14.97	0.00	825.87	27.57	3.78	15.54	52.77	60.60
1:20	172.4	52	19.3	4.16	132.24	32.96	42.93	397.08	22.22	10.89	9.18	28.74	41.42
1:30	172.9	67	19.3	4.16	186.66	23.17	15.98	288.96	25.06	1.03	11.17	26.01	40.94
1:40	161.6	75	19.5	4.34	162.3	12.98	7.62	373.69	23.90	0.92	7.46	30.75	46.77
1:50	162.9	58	19.1	4.32	149.28	16.24	7.75	170.45	13.16	2.18	4.81	23.86	42.27
1:60	170.8	99	19.1	4.18	209.28	9.13	11.86	156.94	15.20	2.17	6.95	21.64	43.56
Weathered Friable Tar													
1:2	272.6	13.4	17.4	2.49	157.9	1.60	0.55	900.09	9.90	1.95	12.50	21.10	24.90
1:10	247.9	4.5	19.9	2.87	161.2	5.82	0.00	290.32	6.02	1.17	6.75	5.29	3.15
1:20	224.7	126	19.1	3.29	205	4.77	0.00	66.90	3.94	0.98	3.15	4.46	4.91
1:30	228.1	194	19.6	3.25	347.3	2.79	0.75	10.36	6.03	0.96	4.35	6.36	3.93
1:40	224.2	193	20	3.31	333.3	5.20	2.50	123.43	8.31	0.33	2.48	10.54	16.49
1:50	217.9	158	19.4	3.41	272.7	3.78	0.00	8.60	6.14	1.58	4.12	6.00	5.75
1:60	213.1	161	19.7	3.49	273.9	8.11	0.00	26.41	5.79	1.31	6.11	9.14	11.20

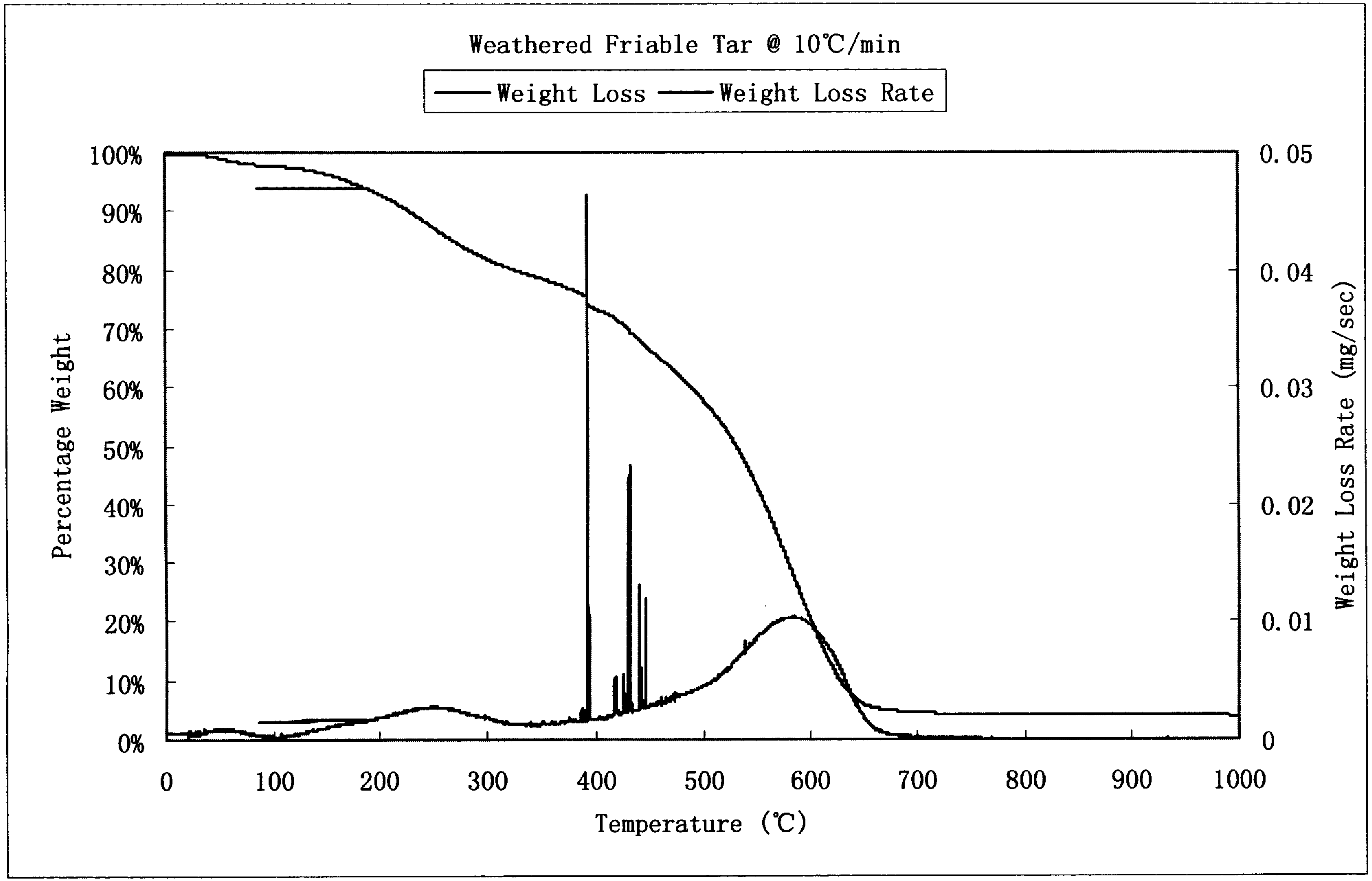
Sample	Conductivity	Turbidity	Temperature	pH	TOC	Chloride	Nitrate	Sulphate	Sodium	Ammonium	Potassium	Magnesium	Calcium
Weathered Crystalline Tar	µS/m		(° C)		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1:2	308.7	8.6	15.2	1.85	104.5	1.76	0.00	902.79	9.70	1.75	12.00	19.75	23.55
1:10	281.5	4.6	20.2	2.37	56.79	1.96	0.00	1509.39	3.03	0.74	2.35	0.68	4.86
1:20	260.1	37	17.9	2.7	33.73	3.73	0.00	599.35	2.63	0.86	1.13	0.67	3.85
1:30	262.1	43	18.4	2.69	45.47	0.98	0.00	537.19	7.80	0.93	2.19	0.47	4.03
1:40	263.9	48	19.5	2.66	43.57	2.64	0.00	672.08	3.46	0.55	2.12	0.47	4.39
1:50	246.1	40	18.5	2.86	40.34	5.28	0.00	318.23	3.01	0.98	1.87	1.55	4.24
1:60	249.9	55	19.5	2.89	279.7	3.05	0.49	8.00	5.49	1.33	4.26	8.08	7.58
Weathered Green Tar													
1:2	290.2	29.8	11.3	2.09	323.6	8.34	1.51	2315.31	9.15	3.10	12.90	15.45	51.00
1:10	266.4	16.3	19.3	2.61	106.9	7.53	0.00	1523.87	1.79	0.02	12.23	0.21	1.36
1:20	231	77	15.4	3.14	62.1	4.81	0.00	205.90	4.41	1.18	1.47	1.67	6.15
1:30	226.1	67	16.9	3.24	56.04	1.49	0.00	101.60	2.86	1.20	1.56	0.67	4.92
1:40	236.3	53	17.7	3.06	51.45	6.01	0.00	118.21	4.76	1.02	5.61	0.47	4.42
1:50	212	51	18.1	3.49	47.95	6.33	1.32	36.95	10.48	1.74	4.80	0.38	1.98
1:60	205.4	48	18.7	3.61	48.37	3.11	1.30	24.12	5.94	1.41	2.41	5.69	5.10
Weathered Black Tar Site B													
1:2	262.9	11	17.1	2.64	73.8	7.93	0.00	787.91	9.05	2.50	6.90	1.15	40.15
1:10	225.7	1.5	20	3.28	64.71	5.65	0.32	116.73	3.95	0.79	3.61	0.31	14.69
1:20	206.8	7	18.1	3.58	51.07	3.91	0.00	64.15	11.35	0.52	2.86	0.51	11.77
1:30	217.7	12	18.4	3.4	65.63	0.30	0.25	85.25	5.18	0.93	2.32	0.26	7.08
1:40	222.7	0	18.5	3.32	89.13	5.90	0.00	94.05	3.38	0.79	1.56	0.25	7.59
1:50	220.3	14	19.3	3.37	83.32	2.54	0.83	90.12	3.91	1.08	1.58	0.30	6.34
1:60	226.4	21	19.7	3.27	100.9	7.08	0.00	139.63	5.47	1.20	2.22	0.39	6.36

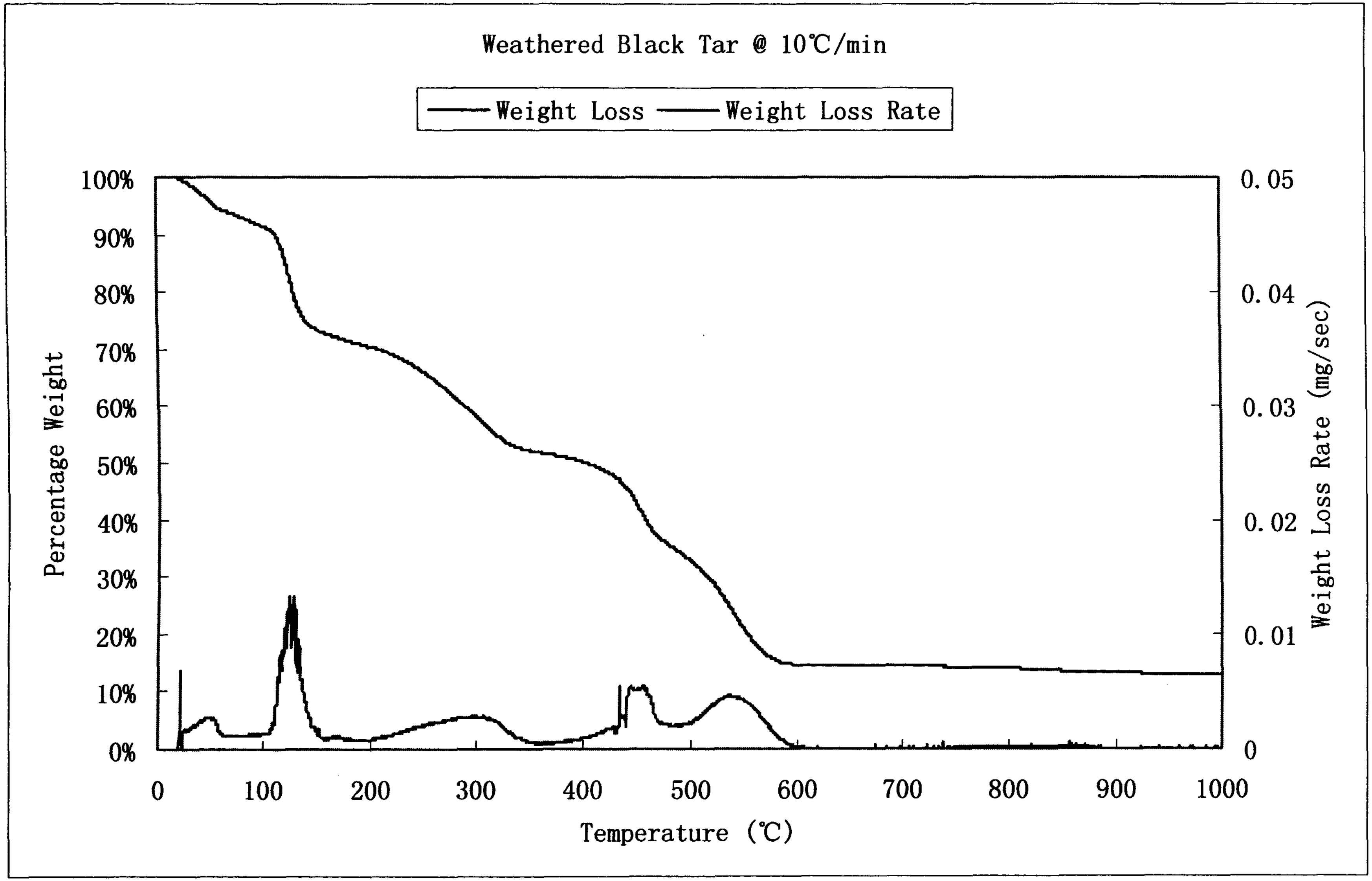
Sample	Conductivity	Turbidity	Temperature	pH	TOC	Chloride	Nitrate	Sulphate	Sodium	Ammonium	Potassium	Magnesium	Calcium
Weathered Friable Tar Site B	µS/m		(° C)		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1:2	225.4	13.9	18.5	3.28	56.37	11.95	0.00	168.73	7.15	3.10	13.45	0.90	10.25
1:10	198.7	4.9	19.7	3.73	27.83	4.36	0.00	45.40	2.29	0.88	3.15	0.96	12.10
1:20	165.7	20	15.7	4.24	18.15	4.02	0.00	17.36	3.61	1.16	2.00	0.52	9.52
1:30	156.3	44	17.6	4.42	23.4	2.98	4.37	14.03	2.62	1.00	2.14	0.20	12.51
1:40	163.8	42	17.7	4.29	25.84	1.67	1.97	15.40	6.50	1.27	2.67	0.32	6.86
1:50	159.6	51	18.4	4.37	31.56	5.71	3.71	13.77	3.86	1.77	4.18	0.46	7.55
1:60	166.2	47	19.5	4.27	21.68	3.89	5.06	19.28	6.04	2.33	2.32	0.45	5.91

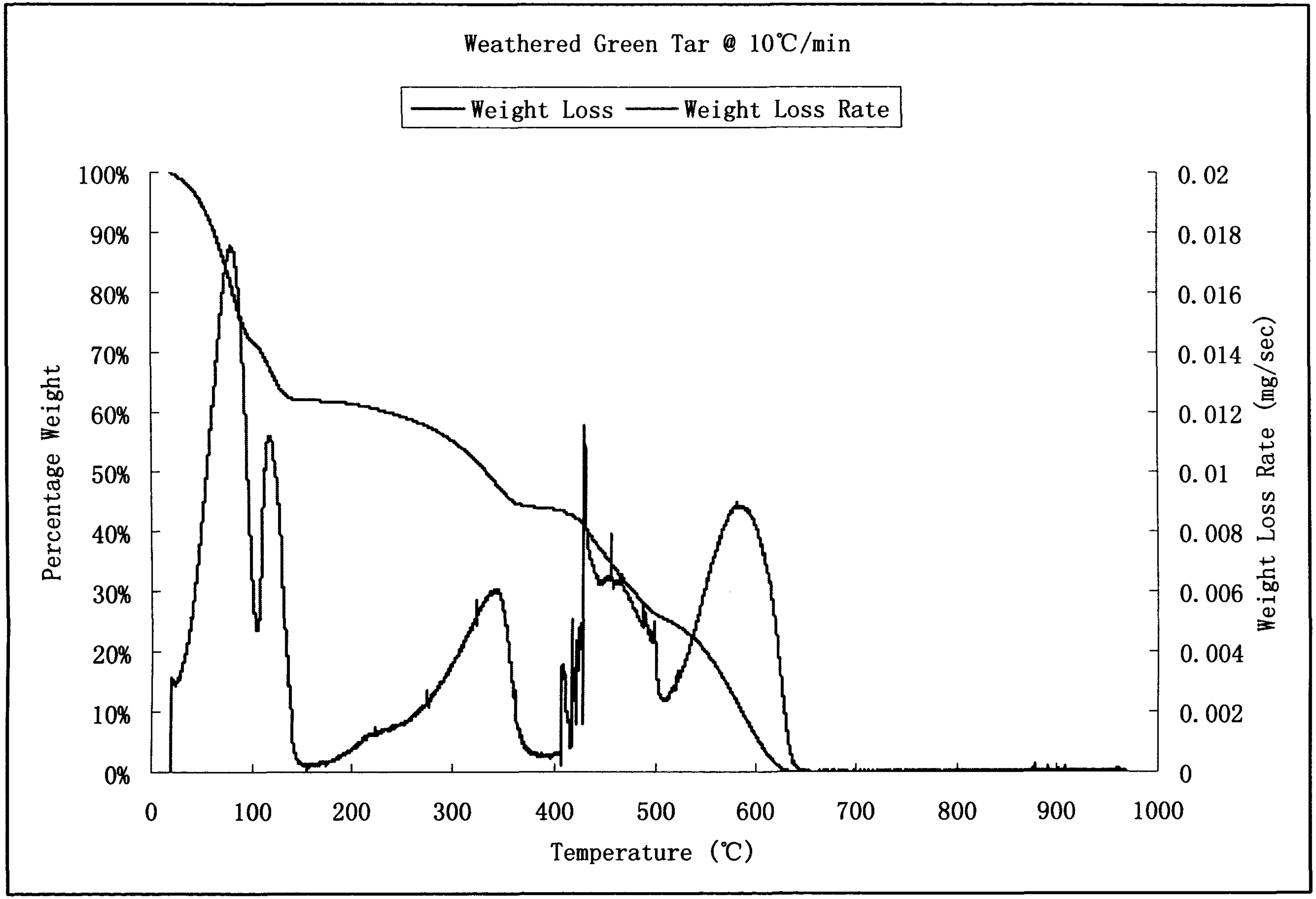
Appendix V TGA analysis

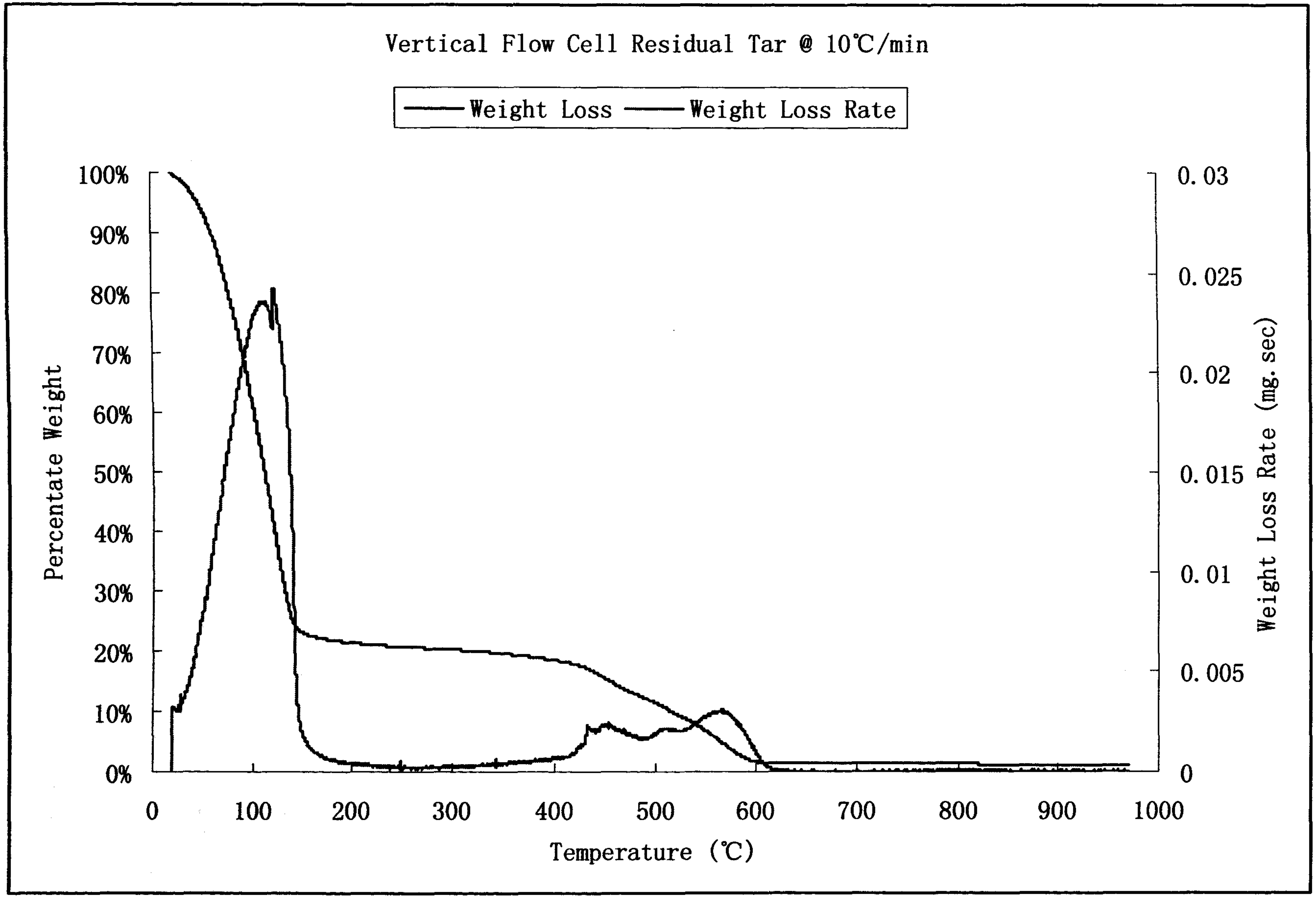



Fresh Tar Grid Temperature Program @ 10℃/min
Weight Loss
Weight Loss Rate
Percentage Weight
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Weight Loss Rate (mg/sec)
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
100
200
300
400
500
600
700
800
900
1000
Temperature (℃)


Weathered Friable Tar @ 10℃/min
Weight Loss
Weight Loss Rate
Percentage Weight
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Weight Loss Rate (mg/sec)
0.05
0.04
0.03
0.02
0.01
0
0
100
200
300
400
500
600
700
800
900
1000
Temperature (℃)


Weathered Black Tar @ 10℃/min
Weight Loss
Weight Loss Rate
Percentage Weight
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0. 05
0. 04
0. 03
0. 02
0. 01
0
Weight Loss Rate (mg/sec)
0
100
200
300
400
500
600
700
800
900
1000
Temperature (℃)


Weathered Green Tar @ 10℃/min
Weight Loss
Weight Loss Rate
Percentage Weight
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
100
200
300
400
500
600
700
800
900
1000
Temperature (℃)
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Weight Loss Rate (mg/sec)


Vertical Flow Cell Residual Tar @ 10℃/min
Weight Loss
Weight Loss Rate
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentate Weight
0.03
0.025
0.02
0.015
0.01
0.005
0
Weight Loss Rate (mg. sec)
0
100
200
300
400
500
600
700
800
900
1000
Temperature (℃)

Appendix VI Physical and Chemical properties of acid tars

9th International FZK / TNO Conference on Soil-Water Systems Bordeaux

Theme G Contaminants

PhD Work: Yes

Physical and Chemical Properties of Acid Tars

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Keywords: Acid Tar

Abstract

Acid tars are dense, viscous tars of high sulphuric acid content that have arisen as by-products of benzole refining, refining petroleum fractions, and oil re-refining. Historically, a common disposal route has been to dump the tars in worked out quarries, clay or gravel pits together with a range of co-disposed materials with little or no pre-treatment and no engineered liner system. The resulting lagoons are of concern due to the physical mobility of the tar and the hazardous nature of particular tar components such as PAHs, BTEX and sulphuric acid.

Containment of the mobile tar often presents problems. It is able to migrate through subsurface fissures and break out onto the ground surface forming relatively thin surface layers. These can weather into several distinct forms, including dust that could migrate through windblow. In the subsurface, contact with groundwater will result in leaching of some of the tar components, while atmospheric pollution potential is present due to the tar's vapour and gas content (e.g. sulphur dioxide and benzene).

Understanding the physical and chemical nature of acid tars is key to predicting their behaviour in the environment and assessing the relative merits of particular remediation options. This paper outlines a range of key issues associated with acid tar lagoon sites and presents work in progress in determining the physical and chemical characteristics of acid

tars relevant to each issue, including pH, density, viscosity and leachability.

1. Introduction

Acid tar is a waste residue of coal and petrochemical processing technologies originating from the end of the 19th century (Milne *et al.*, 1986) but which are now mostly abandoned. There are three main processes that produce acid tars: benzole refining, white oil production and oil re-refining (Nancarrow *et al.*, 2001). Each involves the use of concentrated sulphuric acid as a washing liquid to purify an organic material, which results in a residual tar containing a high proportion of the sulphuric acid. Historically, the methods used for acid tar disposal were mostly by landfill into existing holes or lined lagoons, usually near the former chemical plants. The tar sometimes underwent a limited pre-treatment, and was often co-disposed with other materials leading to the formation of a unique type of brownfield site: acid tar lagoons. The environmental impacts of acid tar lagoons are highly dependent on the nature of the material and the condition of the site. Mechanical instability, gas and volatile emissions, groundwater and surface water contamination, dust blow-off, and direct contact are the most significant hazards associated with acid tar lagoons.

Acid tar is not a homogeneous material. Its characteristics are highly dependent on its production process, its age, the site environment where it is disposed and the presence of any co-disposed materials. Most recent work on acid tars has been focused on ex-situ remediation strategies (Gruss, 2005, Pensaert, 2005, Slater, 2003, Grajczak 1995). This paper reports on work in progress focused on establishing more clearly the physical and chemical properties of acid tars and how they influence the interaction of acid tar lagoons with the environment. This will assist in improving site assessment and in the development of sustainable remediation options.

This work forms part of a PhD investigation within a multidisciplinary research project that focuses on the technical and social-economical aspects of acid tar lagoon problems. The project is looking at tars from a range of UK sites. However this paper focuses primarily on physical and leachability properties of acid tars from one site: Lagoon A in the north of England (location confidential), together with data from the literature. Lagoon A contains acid tars produced by an oil re-refining process. It is contained in an old clay pit and has largely crusted over, with a shallow lagoon of acidic water above the crust. The samples discussed below were taken from the surface or from shallow depth and comprised a range of different forms, mainly due to weathering (Table 1). Top water and near lagoon soil samples were also obtained.

Table 1. Description of acid tar samples

Liquid Tar	liquid acid tar samples obtained from a location of upwelling tar adjacent to the main lagoon
Odourous Liquid Tar	liquid acid tar with significant acidic smell obtained from an upwelling tar location adjacent to the Liquid Tar sampling location
Semi-solid Tar	Semi-solid tar sampled from a tar upwelling location adjacent to the main lagoon. The tar is not exposed at the surface and not fully weathered.
Weathered Particulate Tar	black, powdery, dry weathered tar from a dry, crusted over upwelling location adjacent to the main lagoon.
Weathered Green Tar[1]	green colored, clay like weathered tar obtained from the hard crust of the main lagoon under the ponded water.
Weathered Black Tar[1]	black, clay like weathered tar obtained from a dry, crusted over upwelling location adjacent to the main lagoon.
Lagoon Top Water	acidic water samples from the water ponding above the main lagoon.
Soil	soil samples obtained from a small 'peninsula' protruding onto the main lagoon, below the level of the ponded water.

[1] It is possible that the weathered green and black tars result from an attempted remediation process at the lagoon such as addition of Fullers earth or lime. However historical records are not clear enough to confirm this.

2. Physical Hazards and Tar Properties

2.1 Issues

Acid tars are able to migrate on the surface or through fissures distances of tens of metres from their original locations given suitable driving forces. The rate and distance of migration will primarily be determined by the tar density and viscosity together with any external driving forces e.g. overburden pressures from a capping layer. Density, viscosity and surface tension properties will also be key issues in determining the stability of capping layers and the ability of the tar to migrate into soil pores. Results of initial density tests are reported below together with data from the literature. Measurement of viscosity and surface tension properties is ongoing. No data on surface tension has been found in the literature.

2.2 Density

The density of acid tars varies from site to site. Generally speaking, acid tar is heavier than water but lighter than soil. The density of acid tar is also often higher than typical coal tar at 1060 kg/m^3 (Oudijk and Coler, 1995). High acid tar density is due in part to the high sulphuric acid content (density 1960 kg/m^3). Initial laboratory density tests of acid tar samples (as shown in Table 2) have been carried out by using the British Standard Immersion in Water (BS1377: Part2:1990:7.3) method for measuring soil density. The results show that the Weathered Particulate Tar has a slightly higher density than the Liquid Tar, which it is hypothesized is due to the loss of volatile components during the weathering process. This will be investigated in further laboratory work. The experimental values presented here are much lower than values reported in the literature (as shown in Table 3) and may be attributed to different acid tar production processes. It is clear that tar densities are highly specific to the particular tar deposit.

Table 2. Density of acid tar samples (current work)

Sample Name	***Density(kg/m^3)***
Liquid Tar	1070
Weathered Particulate Tar	1140
Weathered Green Tar	1060
Weathered Black Tar	1020

Table 3. Density of acid tars (from literature)

Source	***Density(kg/m^3)***
Frolov *et al.* (1980)	1160-1430

Nancarrow *et al.* (2001)	Approx 1300

2.3 Viscosity

Acid tars are a thixotropic material with strongly temperature sensitive viscosity. Very limited data is available in the literature on viscosity. Frolov *et al.* (1980) presents some data as illustrated in Figure 1.

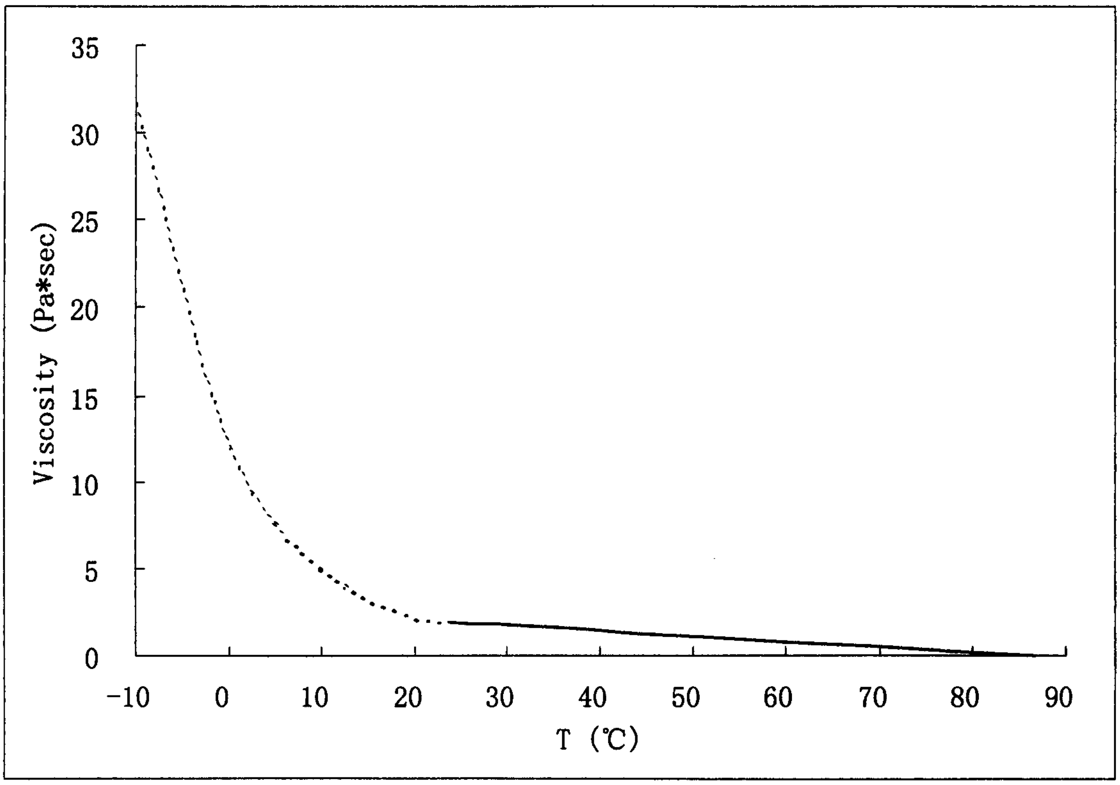

Figure 1 Viscosity data derived (solid line) and extrapolated (dashed line) from Frolov et al. (1981).

2.4 Discussion

Acid tars have a density greater than water but less than most soils. Thus water will always pond on top of the tars, but on those sites which are capped, the density difference between tar and the capping layers can lead to instability problems. A heavier capping layer will pressurize the lighter tar, which encourages the tar to migrate through fissures wherever possible. If migration is vertically upwards, the driving pressure will be sufficient to drive the tar significantly beyond the surface. For example a 1m cap of soil of density $20kN/m^3$ could drive a tar of density $1100kN/m^3$ to a height of 0.8m above the surface. This explains unusual observations seen on several capped sites of undulating topography where the tar is often, paradoxically, seen breaking out onto the surface at the points of highest elevation.

The high temperature dependence of the viscosity indicates that the acid tar is more likely to migrate in the summer than in the winter. Table 4 shows an order of magnitude rate calculation for acid tar migration through a 10mm diameter pathway over a distance of 10m with 2m driving head using the Liquid Tar density from Table 1 and the viscosity data in Figure 1. The calculation is based on a simple Poiseulle flow equation. Flow can easily vary by a factor of 10 between summer and winter. Based on these rates flow could approach 10m^3 in a year through a small fissure. However compounding issues include the weathering and stiffening of the tar as it exits the fissure thus restricting flow.

Table 4. Estimated flow rate of acid tar through a 10m long, 10mm diameter fissure at different temperatures

T (°C)	Viscosity (Pa.sec)	Flow rate (m^3/hour)
-10.00	32	0.001
0.00	12	0.002
10.00	5.0	0.004
20.00	2.1	0.009

Further investigations are required to identify the mechanism of the density difference between Liquid tar and weathered tars and the dependency of acid tar viscosity on the volatile components and moisture content of the tar.

3 Leachability

3.1 Issues

The leachability of acid tars is a key issue controlling the contamination of surface and groundwater. Since the tar typically forms a coherent bulk source, processes at the tar/water interface will dominate the leaching process. Key issues to resolve include:

- chemical and physical determination of water leachable components,
- physical, chemical and transport properties of fresh and leached tar,
- mechanism of continued delivery of leachable components to tar/water interface (e.g. diffusion from fresh tar through the leached tar, direct migration through fissures in the leached tar or via bulk movement of the tar re-exposing fresh tar directly to the ground/surface water),

- role of gas migration (e.g. SO_2).

Depending on the nature of the interaction there may be a first flood of contamination followed by a rapidly diminishing leachate load, or alternatively a relatively steady release of contaminants.

3.2 Batch tests

Batch leaching tests at a water solid ratio of 10:1 were undertaken. Each sample underwent agitation for a period of 24 hours followed by a settling period of 24 hours. During the test procedure, the Liquid and Semi-solid tar samples broke up into colloidal size particles to form a suspension. Prior to analysis the leachate was centrifuged at 8000rpm for 10 minutes and then filtered through 0.45um filter paper.

The pH and Ion Chromatography (IC) analysis of the leachates are shown in Table 5. The Odourous Liquid Tar clearly contains high levels of sulphuric acid as it yields the lowest pH and the highest sulphate content. The Liquid Tars and other weathered tars produce similar pH leachates and sulphate concentrations of ~1000ppm, however the weathered tars all have significantly higher levels of leachable calcium which may indicate some form of lime treatment in the past.

HPLC analysis on leachate has been undertaken to identify the presence of phenols. However the results indicate the phenol concentration is below the detection limit. Therefore the phenol concentration is very low on this lagoon.

For comparison purposes, an IC analysis of the lagoon top water is given in Table 6, and shows similar orders of magnitude of concentrations as the Liquid and weathered tars. The pH level was also similar at 2.84 (measured on site at a temperature of 12.2 °C). However the Odourous Liquid tar (as mentioned above) has a significantly higher sulphate concentration and lower pH. Rigorous correlation of the top water and batch test data will require a model of tar/water interaction and knowledge of the rate of replenishment of the water by precipitation and loss through overspill.

Table 5. pH and IC analysis of leachates

Samples	***pH***	***T***	***Na***	***K***	***Mg***	***Ca***	***F***	***Cl***	***SO_4***
		(°C)	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Liquid Tar A	2.25	24.1	26.84	21.00	146.24	19.54	4.06	32.82	1422.21
Liquid Tar B	2.32	24.5	28.56	19.41	150.75	21.39	<3.00	30.81	1458.89
Odourous Liquid Tar A	1.66	22.3	37.61	38.68	336.56	12.51	7.94	40.43	8381.33
Odourous Liquid Tar B	1.62	24.2	37.76	40.58	344.17	13.77	7.30	36.74	8347.49
Semi-solid Tar A	2.34	21.1	24.03	13.15	151.09	17.62	3.77	26.00	1187.66
Semi-solid Tar B	2.40	23.3	25.96	12.79	148.46	16.64	3.96	27.67	1191.32
Weathered Particulate Tar A	2.40	21.0	21.25	<6.00	<6.00	<12.00	<3.00	21.39	653.01
Weathered Particulate Tar B	2.35	24.4	50.76	9.08	<6.00	39.27	<3.00	46.16	511.83
Green Weathered Tar A	2.34	21.2	89.25	20.47	125.18	109.83	<3.00	19.92	2869.56
Green Weathered Tar B	2.24	24.2	85.16	21.80	128.60	113.47	3.16	18.19	2818.97
Weathered Black Tar 1 A	2.45	24.0	86.36	28.98	167.30	219.01	3.35	20.29	2945.41
Weathered Black Tar 1 B	2.45	22.1	89.10	27.28	173.03	219.94	3.09	20.70	2916.52
Weathered Black Tar 2 A	3.32	23.5	34.46	12.16	84.34	224.26	<3.00	22.63	1454.46
Weathered Black Tar 2 B	3.27	21.2	32.42	11.51	86.99	230.73	<3.00	20.00	1429.37
Soil A	6.80	22.1	26.85	<6.00	8.10	255.24	<3.00	16.96	599.39
Soil B	6.94	23.6	18.13	<6.00	6.30	401.98	<3.00	18.18	837.76

Note: 1.Sample A, B stand for duplicate tests carried out for the same type of sample.

2. Weathered Black Tar 1 and 2 are same type of tar but sampled from different location.

Table 6. Lagoon surface water IC results

Sample	***Na***	***K***	***Mg***	***Ca***	***F***	***Cl***	***P***	***SO_4***
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	27.73	4.07	23.51	28.05	0.87	12.06	0.25	764.03
2	27.86	4.12	22.15	25.24	0.73	12.36	1.76	772.37
3	28.25	4.68	20.60	23.79	0.92	12.32	8.78	760.55
4	28.02	4.65	22.27	26.53	0.60	11.96	5.72	752.46

5	27.91	4.21	23.37	27.25	0.65	12.66	2.95	762.70
6	27.59	4.31	23.33	26.60	0.90	12.08	2.45	769.22

Table 7 presents the results of Total Organic Carbon (TOC) analysis on the leachate as an initial indicator of water soluble organics. The Liquid and Semi-solid acid tar samples have significantly higher TOC values than the weathered tar samples,

Table 7. TOC result of leaching test

Sample Id	***mg/l***
Liquid Tar A	2329
Liquid Tar B	2469
Odourous Liquid Tar A	3389
Odourous Liquid Tar B	3810
Semi-solid Tar A	2483
Semi-solid Tar B	2163
Weathered Particulate Tar A	311.35
Weathered Particulate Tar B	291.75
Green Weathered Tar A	267.40
Green Weathered Tar B	285.30
Weathered Black Tar 1 A	407.15
Weathered Black Tar 2 B	326.15
Weathered Black Tar 2 A	239.90
Weathered Black Tar 2 B	228.35
Soil A	32.31
Soil B	34.50

Notes: 1.Sample A, B stand for duplicated test carried out for same type of sample.

2. Weathered Black Tar 1 and 2 are same type of tar but sampled from different location.

3.3 Discussion

The batch leaching tests show that the liquid, semi-solid and weathered tars leach significant quantities of both organic and inorganic components. Sulphuric acid is clearly leached and its persistence and fate in ground and surface water requires further attention. Unweathered tars leach significantly lower levels of TOC than the weathered tar, which would indicate that the acid tar loses many of its mobile organic components during the weathering process, presumably through leaching, loss of volatile organic hydrocarbon or the oxidation of some water soluble compounds. Specific analysis of organic leachate components is planned in the next phase of investigation and requires careful consideration of suspended matter; the analysed leachate contained a proportion of fine particles, but had particles removed which may be mobile in a coarse grained soil. Column tests will be essential in investigating leaching processes in detail and to ascertain whether leached organic components are released in a first flush leaving a relatively inert tar behind. Implications from the weathered tars are that a large proportion of organics are lost on leaching, though this is not the case for the sulphuric acid.

4. Conclusions and further work

4.1 Conclusions

- The physical properties of acid tar have a significant influence on the stability of acid tar lagoons. The density difference between acid tar and a capping soil is one of the driving forces for tar migration on a capped site. The rate of tar migration is controlled by the viscosity which is significantly temperature dependent. Significant volumes can migrate through very small pathways over a period of months.
- Batch leaching tests indicate that acid tar has significant quantities of organic and inorganic leachable components. Sulphuric acid is clearly leached and its persistence and fate in ground and surface water requires further attention. TOC measurements also indicate significant leaching of organic components from fresh liquid tars, while significantly lower levels are observed in weathered tars. In contrast leaching of sulphuric acid from weathered tars is often comparable to that from unweathered specimens, indicating that while there may be a first flush of organic leachate, sulphuric acid will be released more steadily.

4.2 Further work

The analysis to date has mainly focused on the inorganic components of the tar. The organic part of the problem is more complex. Full chemical composition analyses are scheduled for selected tar samples together with an organic analysis of leachates.

More realistic column leaching tests will be carried out based on the batch test results. Additional batch leaching tests with adjusted conditions (shaking time, water-solid ratio, temperature etc.) are also planned.

Weathering trials are being designed and implemented to address how the acid tar transforms under different conditions. The nature of each weathering form will be fully studied. It is possible that a certain weathered form could become part of a potential remediation solution.

By characterising acid tars, physically and chemically, the environmental impacts of acid tar lagoons will be better understood, and should contribute to the sustainable remediation of acid tar lagoons.

Acknowledgements

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Appendix VII Site visit reports

Hoole Bank Acid Tar Lagoon Site Visit Report

Date 22 July 2004

1. Site plan and locations.

Hoole Bank Acid Tar Lagoon is located north east of Chester, near the A65. It is a fenced site with restricted access. The site is surrounded by grassland and farmland. The nearest residential propertu is more than 100 meters away from the site.

A detailed site plan is givenl in Appendix I. The site entrance is at the North West corner of the site. Five sample locations are marked as follows:

Location A: Adjacent to the water treatment chambers

Location A1: Just south of the water treatment chambers, along the track where at the location of a tar bleed.

Location B: On the bund at the SE corner of the lagoon.

Location C Further round the lagoon at the location of a tar bleed

Location D: a large tar bleed loaction

Location E: Adjacent to the old overflow pipe that led to the adjacent landfill

2. Diary of activities, weather, temperature and samples taken.

Weather and temperature: cloudy day with little rain in the noon, temperature 25-30° C

Samples, measurements and observations are listed below.

Location A and A1:

Surface water (clear) pH: 2-2.5 (all the pH value on site are tested by indicator paper)

2 clear water samples and 2 brown water samples

1 shallow depth tar samples (approximately 0.2m underground) and 1 surface hard weathered tar samples

Location B:

Surface water pH 2-2.5

2 clear water samples, 1 brown water samples,

Location C

- A frog is found near the tar lagoon .
- Probings indicate that a hard crust appears to be present beneath the surface water
- Vegetation present on small islands within the lagoon. The vegetation looks unhealthy (yellow leaves). The soil on the island has a black coating.
- pH of the top water is 2.5 and pH of the liquid (rain water) that had ponded on a surface tar bleed was 1
- 1 surface tar sample from the tar bleed
- 1 soil sample under the vegetation and 2 soil samples near the tar lagoon
- 1 liquid sample from the surface tar
- 1 shallow sample from the tar bleed and 2 weathered tar samples along the tar flow direction (1 in the middle and 1 in the end)

Location D:

- Open tar surface arising from tar bleed, hard crust on most places but some part of the surface is very soft. Various weathered tar forms are found at this location including hard black weathered tar on the surface, black powdery (friable) weathered tar on the surface and green solid weathered tar at shallow depth. Following excavation of a hole on the soft part of the tar crust (about 10cm deep), the hole filled with fresh liquid tar again after 30 minutes.
- 2 friable weathered tar samples
- 2 tube fresh tar samples
- 1 flowing tar (semi-fluid fresh tar)
- 1 original weathered tar
- 1 tar/soil mixture (near a cutting surface of a tree root zone, looks like green surface tar)
- 2 fresh tar samples (1 at the location of the tube samples and 1 further into the woods, which smell quite acidic nearby)

Location E:

2 green weathered solid tar samples under water (excavated)

Hoole Bank Acid Tar Lagoon Site Visit Report

Date of Visit: 15 June 2005

Location: Hoole Bank acid tar lagoon, Off The Street, Hoole Bank, Chester

Weather: Cloudy, light rain at midday

On-Site Activities and Sampling:

Site walk through, pH measurement of surface water, hand held (Perth) penetrometer test at various locations, migration measurement of excavation from previous visit, surface sampling, penetration sampling

Sample and penetrometer test locations:

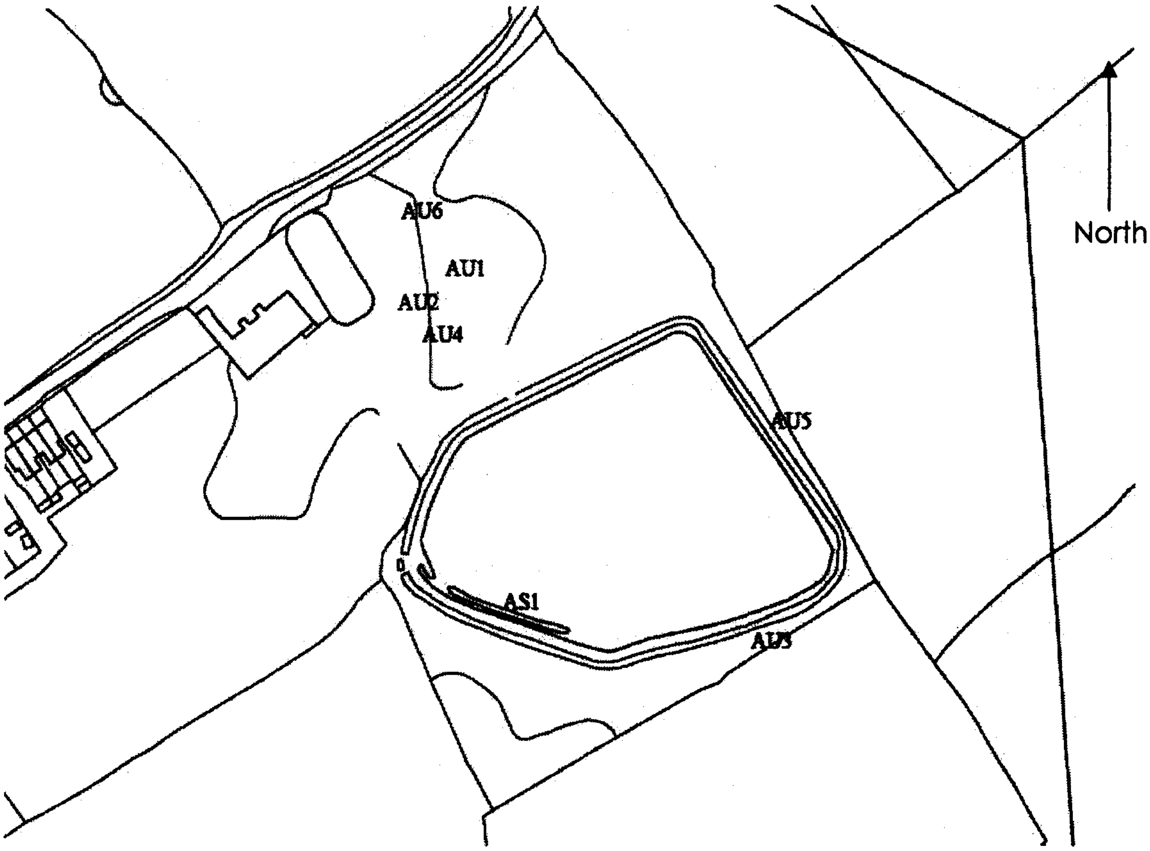


Fig 1 Site plan of Hoole Bank Acid Tar Lagoon

Location 1: At the north edge of a major tar bleed location, near a fresh tar upwelling point.

Location 2: South of the fresh tar upwelling point, in the middle of the tar bleed.

Location 3: At the south part of the major tar bleed location, where there is no tree coverage and is wetter than the location 1 & 2.

Location 4: At the west part and highest point of the major tar bleed location,

Location 5: At the north east corner of the main acid tar lagoon, covered with shallow surface.

Samples:

Sample ID	Description	Location
AT01	Tar sample under crust (semi-liquid)	AU4
AT02	Core sample of the crust	AU4
AT03	Dry green weathered tar	AU2
AT04	Tar sample under crust (semi-liquid)	AU4
AT05	Powdered tar	AU6
AT06	Surface Brown and then green weathered tar	AU2
AT07	Surface Powdered Tar	AU2
AT08	Black Rubbery Tar (Clay-like)	AU4
AT09	Black Rubbery Tar near surface	AU4
AT10	Black crystallized tar	AU6
AT11	Black crystallized tar	AU6
AT12	Beige clay like tar (deeper, dry)	AU4

Notes of the visit:

1. pH of surface water: 2.92 at 24.2° C
2. "Pond weed" in the top water is recognized as a bio-film.
3. At location 1: Excavation of dry weathered tar shows a three layer structure: black friable tar at the top, dark green tar in the middle and black crystallized tar further down. There is no distinct interface between layers.
4. At location 2: Find clay like, rubbery tar which is very flexible and has more moisture content. There was 5-10 cm surface water at this location during the preceding visit (Nov. 2004) but the water has drained this time and there are cracks on the tar surface.
5. Penetration test and sampling adjacent to the bank of the main lagoon indicates there is no distinct transition to liquid tar under the crust. The deeper tar is semi-liquid and flexible.

Appendix:

I. Penetrometer Tests (blows per cm)

Location	**1**	**2**	**3**	**4**	**5** (surface water depth 15cm)
5cm	3	1	6	3	2 (20cm)
10cm	4	1	6	5	3
15cm	6	1	7	6	2
20cm	6	1	5	6	2
25cm	5	1	6	5	1
30cm	5	2	3	6	2
35cm	3	1	4	6	1
40cm	3	2	4	7	1
45cm	5	1	6	7	1
50cm	4	1	7	6	1
55cm	4	1	5	5	1 (85cm)
60cm	5	1	6	6	
65cm	6	2	7	8	
70cm	5	5	8	5	
75cm	5	2	8	6	

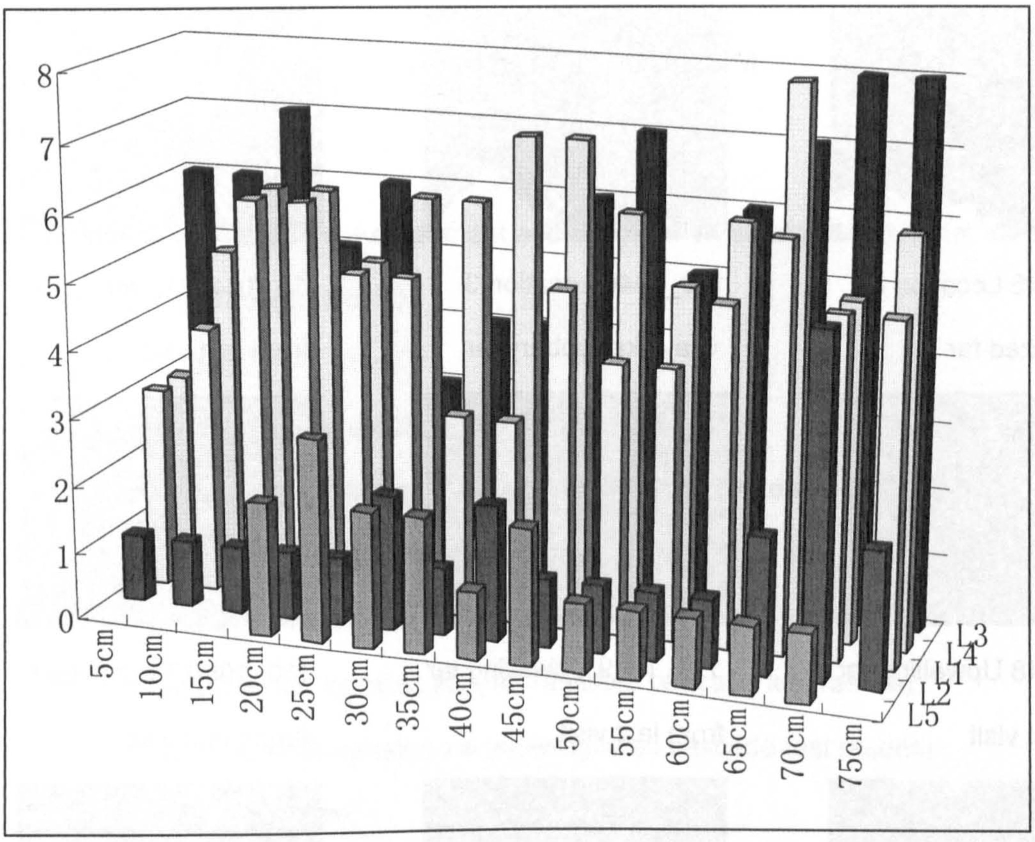


Fig A1. Penetrometer tests (blows per 5cm penetration)

II. Photos

110_1039 Location 1

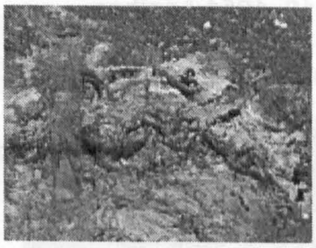
Powdered and Green

Weathered tar

110_1040 Location 1

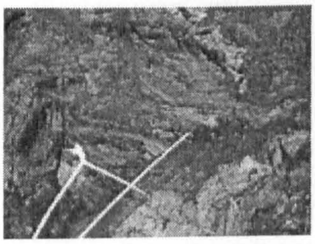
Deeper crystallized

black tar



110_1041 Location 1

Cross section



110_1042 Location 1

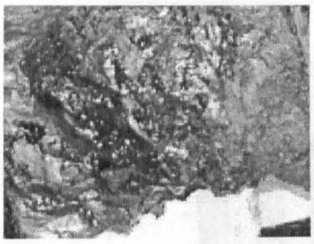
Cross section

110_1043 Location 1

Cross section

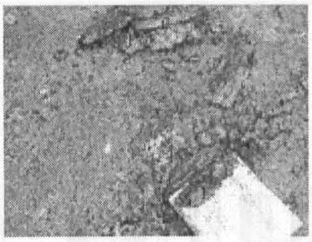
110_1044 Location 2

Surface dry tar



110_1045 Location 2

Crystallized tar

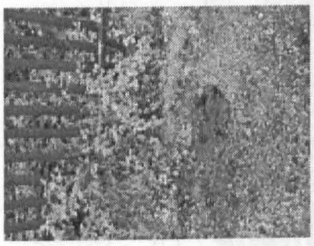


110_1046 Location 3

Clay like rubbery tar

110_1047 Upwelling tar

from last visit



110_1048 Upwelling tar

from last visit

110_1049 Upwelling tar

from last visit

110_1050 Tar cleaned

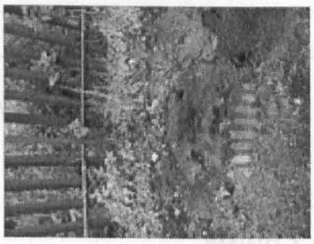
during last visit

110_1051 Another

upwelling tar

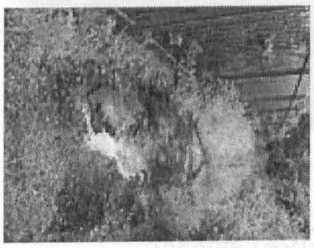
110_1052 Another

upwelling tar



110_1053 Another

upwelling tar



110_1054 Another

upwelling tar

110_1138 Location 1

surface powdered and

green weathered tar

Appendix VIII CD-ROM

File List:

--Thesis, Acid Tar Lagoons, Assessment and Environmental Interaction, Final Version.doc

(Electronic version of the thesis)

--Data (data folder)

--------icp.xls (ICP analysis results

--------verticalflowcell.avi (Imaging video of vertical flow cell)

--------leaching (leaching test data folder)

----------------batchtest.xls (batch leaching test results)

----------------cascade non-agitated.xls (non-agitated cascade test results)

----------------cascade slow-agitated.xls (slow-agitated cascade test results)

--------*TGA (TGA data folder)*

----------------viscous tar scanning.txt (viscous tar scanning temperature program results)

----------------viscous tar grid.txt (viscous tar grid temperature program results)

----------------weathered friable tar scanning.txt (weathered friable tar scanning results)

----------------weathered black tar scanning.txt (weathered black tar scanning results)

----------------weathered green tar scanning.txt (weathered green tar scanning results)

----------------vertical flowcell residual tar scanning.txt (flowcell residual tar scanning results)