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MASTER OF SCIENCE THESIS

**ABSORPTION MATS FOR OIL
DECONTAMINATION**

Towards Sustainable End-of-Life Tyre Management

ARONU, UGOCHUKWU EDWIN

X050049@UTB.HB.SE

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ARONU, UGOCHUKWU EDWIN

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University College of Borås
School of Engineering
SE-501 90 BORÅS
Telephone +46 033 435 4640

Examiner: Professor Mikael Skrifvars

Supervisor: Tatjana Karpenja; Futurum Recycling AB

Client: Futurum Recycling AB, Gothenburg

Work City Borås

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SUMMARY

It has become imperative globally that we build a more sustainable society. Part of the drive towards attaining this includes finding an environmentally friendly solution to materials we use including materials from automobile vehicles. This research is focused on finding a sustainable solution to end-of-life tyres through material recycling into useful products; in this case absorption mats for oil decontamination from tyre rubber granulate.

The research consisted of two parts. Firstly, theoretical reviews which involved an extensive literature review of oil decontamination practice and methods of doing it. Review of tyre rubber granulate properties and consultations with experts/agencies involved in oil decontamination operations in Sweden where mostly physical methods such as use of absorbents on land and booms on water. The second component of the research is an experimental part which involved laboratory test of the absorption properties of tyre rubber granulate at University College of Borås (HB) in which granules of sizes 0.50, 1.00 and 2.00 mm were tested on different oil samples; gasoline, diesel and motor oils. Environmental properties tests were also conducted at the Swedish Technical Research Institute (SP) where metal and organic contents of the granules and its leachate were tested.

Results from the study showed that tyre rubber granules have the ability to absorb different types of oil. It was found that factors such as exposure time, granulate size, temperature and type of oil have effect on the absorption capacity of granulate. Highest absorption (2.518 g/g) was experienced with the least viscous oil; gasoline. Absorption was found to increase with an increase in temperature and decrease in granulate size with the smallest granulate size (0.50 mm) having the highest absorption at 30°C. It was equally observed that the presence of water does not have significant effect on oil absorption by granulate. The results also showed that tyre rubber granules are quick absorbents; absorption rate was highest within 5 minutes.

Environmental properties test on granulate indicated the presence of organics (PAHs, phthalates, phenols) and metals (Pb, Zn, Cr, Cd) in granulate and its leachate. PAHs content of the granules and its leachate exceeded the Swedish guideline. Metal content of the granules and its leachate were below the guideline value with the exception for zinc (Zn) which content in granules exceeded guideline value. It should be noted however that the test conditions are too extreme to be experienced under normal condition of use of granulate for oil decontamination.

It is concluded that tyre rubber granulate can be developed into absorption mats for oil decontamination due to its good oils absorption properties and benefits to the society in solving two key environmental problems; oil spill and tyre waste problems. Equally the use of tyre granules for this application will not pose human health and/or environmental risk if used adequately.

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1. INTRODUCTION

1.1 Background

The increasing trend in the world's industrialization has resulted in increase in social facilities including automobile vehicles. The increase in number of automobile vehicles on our roads globally has also led to an increase in the number of used tyres dismantled from such vehicles. In year 2006, the European Tyre Recycle Association reports that the global annual tyre waste generation stands at about one million tonnes. Considering the huge resources involved in the manufacture of this mass of tyres annually, it has become pertinent that tyres should not be considered as waste. This thus calls for more innovative approaches for the management of used tyres. Environmental friendly solutions must be developed for used tyres if we must remain in the track for sustainable development since tyres themselves have become a problem to the society.

Sustainable development on its part is that development that involves economic activities that meet the current social needs without threatening the capacity of future generations to meet their own needs. To build a more sustainable society, materials of the future must meet the conventional criteria of high performance and low cost with commitment to human safety and environmental protection. A sustainable material management involves two key strategies: dematerialization and detoxification; these will offer avenues for achieving a safer and more environmentally protective future. Dematerialization on the other hand involve; reusing materials, recycling, designing products that use fewer materials or substituting nonmaterial services for material-intensive products (Geiser, K., 2001).

This research is focused on material recycling of end-of-life tyres as a dematerialization method. This is the next best option after reuse in the hierarchy of waste management for a more sustainable automobile vehicle tyre management. The research views used tyres as a valuable resource rather than a waste material, thus it is directed at developing of useful products from end-of life tyre, and in this particular work on developing of absorption mats for oil decontamination from used tyres.

1.2 Tyre Composition

A tyre is a rubber article with a complex structure. It is a composite consisting of materials with different properties. Figure 1.1 gives an illustration of the structure of a tyre. The figure shows that tyre is an advanced engineering material made of a lot more than a rubber. Other materials present in tyre include fibres, textile and steel cord. These components go into the tyre's innerliner, body plies, bead assembly, belts, sidewalls, and tread (Maxxis, 2007).

Due to its intended use, a wide range of chemical compounds can be found in the tyre rubber of road vehicles. About forty percent of tyre is rubber. Other substances that are used in relatively large amounts in tyres are carbon black (reinforcing agent), aromatic oils (plasticizers), sulphur (vulcanizing agents), zinc oxide (activators); several metals are

also used (KemI, 2006). Alkyl phenols are used as antioxidants to protect the material from breakdown due to reaction between the polymers and the oxygen in air.

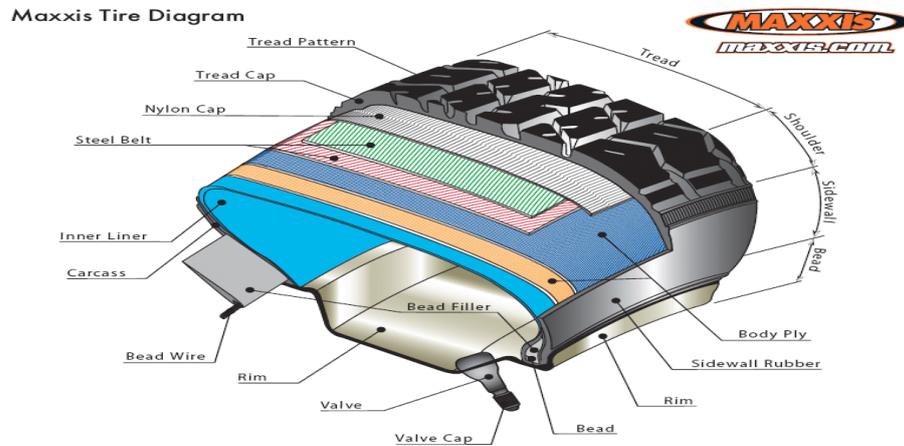


Figure 1.1 Structure of a Tyre. Source: Maxxis International, 2007.

The material composition of tyres in the European Union as was presented in the Basel Convention, 1999 is shown in Table 1.

Table 1: Material Composition of Tyres in the EU; Source: Basel Convention, 1999.

Material	Passenger Car	Truck
Rubber /Elastomers	47%	45%
Carbon black*	21.5%	22%
Metal	16.5%	25%
Textile	5.5%	--
Zinc oxide	1%	2%
Sulphur	1%	1%
Additives	7.5%	5%

* Part of the carbon black may be replaced by silica in certain types of tyres

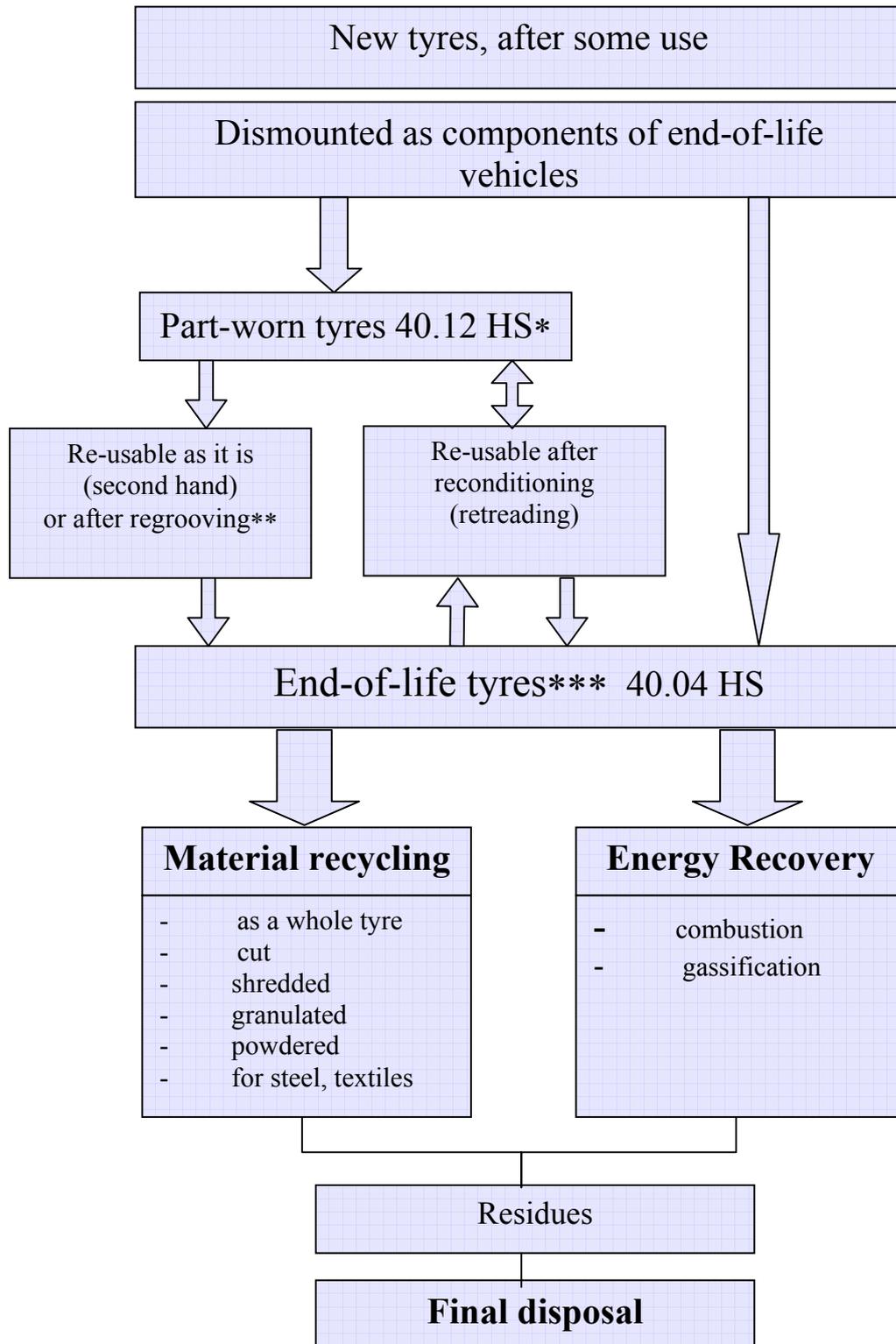
1.3 Tyre Management

Tyres as can be seen are very crucial part of automobile vehicles; however at the end of its service life, if it not properly managed, it could be a problem to the environment.

Tyres removed from vehicle after some use could be part worn tyres or end-of-life tyres.

- Part worn tyres are tyres which are re-usable as it is (second-hand) or after regrooving and also tyres which are reusable after reconditioning (retreading).
- End-of-life tyres on the other hand are non-reusable tyres, which goes to other management options. Part worn tyres eventually become end-of-life tyres also.

Figure 1.2 is an illustration of the different categories of used tyres and various stages of stages in the life of a tyre as presented in Basel Convention, 1999; report on used tyres.



* HS stands for harmonized customs code system
 *** Scrap tyre is an equivalent term used in the USA

** Regrooving for truck tyres only

Figure 1.2: Identification of Different Categories of Used Tyres

Source: Basel Convention, 1999.

European Tyre Recycle Association (ETRA), (2006); reports that about ±300,000,000 tyres reach their end-of-life each year in the 25 Member States of the European Union, this amounts to an annual accumulation of about ±2,978,296 tonnes of tyre in the EU; of this Sweden generates about 70,000 tonnes. It further stated that similar amounts are found in North America, Latin America, Asia, and the Middle-East. It puts the global total to be ±1,000,000,000 new arisings of end-of-life tyre per year.

For many years these tyre accumulations have been managed by methods which cannot be classified as sustainable. Many were stockpiled or buried in designated landfills; many are found in illegal dumping sites, warehouses, mountains, valleys etc. In order to put an end to such unsustainable practices, the EU has put in place a number of directives to promote a more sustainable end-of-life tyre management. The directives are as follows:

- *The Directive on PAHs in Tyres (2005/69/EC) of 16 November 2005*: This directive places restriction on the use of High Aromatic (HA) oil in tyres manufacture; this has been the main concern in use of tyre for other products (material recycling of end-of-life tyres). This directive takes effect from 1st January, 2010.
- *The Directive on Incineration of Waste (2000/76/EC) of 4 December 2000*: This directive provides new emission limits for incineration and co-incineration (including cement kilns) plants. The limits are effective for new plants from 28 December, 2002 while old plants are from 28 December 2005. Special provisions was however provided for cement kilns (which often uses tyre for fuel); until 1st January, 2008. By these new limits, it implies that by 2008, tyres may not be very desirable as fuel in cement kilns if the emission limits are to be achieved economically.
- *The Directive on End-of-life Vehicles (2000/53/EC) of 18 September 2000*: This directive lays down measures aimed at preventing vehicle waste through promotion of reuse, recycling and other forms of recovery of end-of-life vehicles and their components which include post consumer tyres. It sets recycling and recovery targets to be achieved by 2015.
- *The Directive on the Landfill of Waste (1999/31/EC) of 26 April 1999*: This directive places restriction on landfilling of whole tyres from 16 July, 2003 and shredded tyres from 16 July, 2006; excluding tyres used for engineering purposes, bicycle tyres and tyres with outside diameter above 1400mm.

The European Union strongly encourages maximum material recovery of waste in its 'Thematic Strategy for prevention and recycling of waste' as a means of improving the sustainable use of resources within the EU. The long term goal is for the EU to become a recycling society, organized around the maximum recovery of materials where this makes environmental and economic sense, and energy recovery where this is more efficient, ETRA, 2006.

The management options for used tyres in EU as reported by European Tyres Recycle Association are as shown in figure 1.3 below. 32% of the used tyres undergo recycling while the most common treatment option is energy recovery (34%).

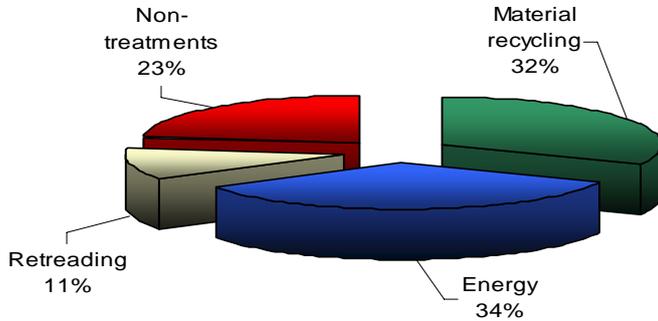


Figure 1.3: Estimates of End-of-Life Tyre Routes in the EU, Year 2006.
Source: ETRA, 2007.

There have been continuous increases in the material recycling of used tyres in the recent past. Figure 1.4 shows the trend in the growth in material recovery of used tyres in EU from 1992 to 2006 as reported by ETRA 2007. The figure shows that in 1992 about 5% of used tyres are recycled, but by 2006 this has increased to 32%.

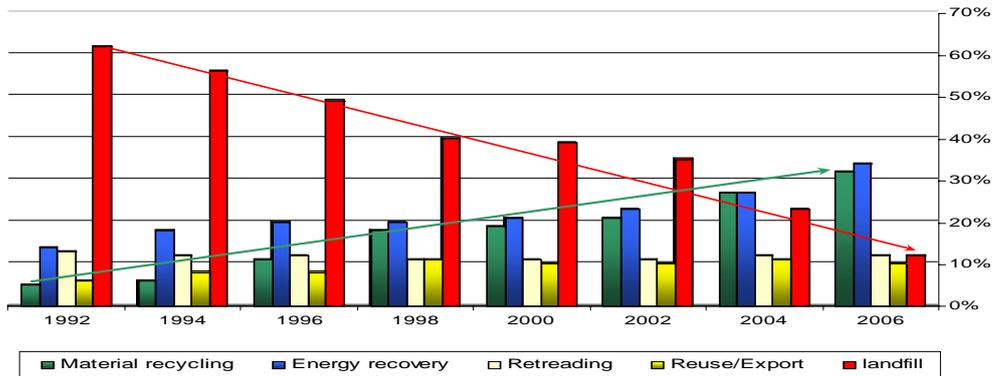


Figure 1.4: End-of-life tyre valorisation routes in the EU, 1992 – 2006. Source: ETRA 2004-2007.

1.4 Reduced In Size End-Of-Life Tyres

For the material recycling of end-of-life tyres, the tyre is either used as a whole tyre or is cut into different sizes depending on the intended application. The tyre fractions are also named according to their sizes. Below is an illustration of some of the different sizes which an end-of-life tyre can be cut and their possible applications (ETRA, 2007)



Shred (50-300 mm) is the result of mechanical treatment to fragment, rip or tear the tyre into irregular pieces 50-300 mm in any dimension.

Principal uses: lightweight fill, backfill, drainage, thermal insulation or roads or buildings, sound barriers, landfill engineering, or as a feedstock.



Chips (10-50 mm) are produced as shred resulting in irregularly shaped pieces of 10-50 mm

Principal uses: backfills, bridge abutments, lightweight fill for construction, drainage, landfill maintenance, road and sports foundations, soil treatments or as a feedstock.



Granulate (1.0 – 10 mm) is the result of processing the material to reduce it in size to finely dispersed particles 1-10 mm.

Principal uses: artificial turf, automotive parts, crash and noise barriers, flooring, paving and roofing supplies, playground and sport surfaces, footwear, soil treatments, soil shells, road furniture and traffic systems, rubberized asphalt, sports, carpet underlays, vibration mats or as a feedstock for further treatment.



Powders (< 1 mm) are the result of processing rubber to achieve finely dispersed particles of < 1 mm.

Principal uses: automotive parts, cable bedding compounds, fillers for tyres, footwear, porous bitumen binders, coatings and sealants, sport equipment, surfacing or as a feedstock for specialized treatments, carbon material, pigments for inks, paints, thermoplastic elastomers.

1.5 Tyre Derived Products and Services

Tyres have been identified as *valuable resource* rather than a waste material. It can be put into several different applications either as a whole tyre, shredded, chips, granulate or powder. Some of the applications of tyre are as follows:

- Mats
- Thermoplastic Elastomers
- Foot wears (Shoe Sole)
- Flooring: Indoor/Outdoor
- Sports Surfaces/Pitches
- Children's Play Areas
- Asphalt Compounds
- Porous Pipes
- Noise Barriers
- Road Construction
- Roofing and Insulation materials
- New tyre manufacture

Figure 1.5 is an illustration of some of the tyre derived products and services.



Figure 1.5: Some Tyre Derived Products. Source: Tyre Recycling Success, 2007.

1.6 Aims of Study

- This study is aimed at promoting material recycling of end-of-life tyres by using them as a valuable resource after granulation, in particular to produce goods or services for the benefit of mankind.
- To investigate the possibility of developing absorption mats for oil decontamination from tyre granulate that possesses good absorption properties.
- To investigate the environmental properties of tyre rubber granules, hence such properties of the absorption mats to be developed.
- To check an economic feasibility of producing the absorption mats.

The unique aspect of this research is that by successful production of absorption mats from tyre granulate and application of this product for oil decontamination, we will be solving two key environmental problems (end-of-life tyres and oil spills) using the problems themselves.

1.7 Scope of Study

This study covers three aspects which are as illustrated in figure 1.6:

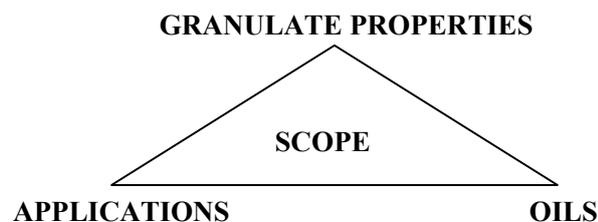


Figure 1.6 Scope of Study

The three aspects of the current thesis work are as follows:

Granulate Properties

This involves study on absorption performance and environmental properties of tyre rubber granulate. The environmental properties entail study on the metals and organic compounds composition of granulate with the emphasis on any potential impact on human health and environment.

Applications

Areas of application covered in this work are: indoor and outdoor uses of absorbent for the purpose of oil spill decontamination; in particular, uses on land and in natural waters such as rivers, lakes etc.

Oils

In this aspect various types of oil (such as diesel, gasoline, and motor oils) that may be encountered in an oil spill decontamination situations are considered. Oils are tested on tyre rubber granulate for absorption performance.

2. OIL DECONTAMINATION

2.1 Oil Contamination

Before any decontamination, there must be contamination. Thus before going into detailed discussions about oil decontamination, this part of the report introduces the concept of oil contamination, equally highlighted are the different types of oil that might be encountered in an oil decontamination exercise; since one of the factors affecting the oil decontamination method to be deployed, is type of oil spilt.

Oil is any substance that is not miscible with water, and is in a viscous liquid state at ambient temperatures (Wikipedia, 2007). To contaminate means to make impure by exposure to or addition of a poisonous or polluting substance (Oxford Dictionary, 2007).

The term oil contamination means polluting by oil discharge to land, water or air and thus harming the environment. Spill on the other hand is to cause or allow to run or fall from a container, especially accidentally or wastefully while leak is an unintended hole, crack, or the like, through which liquid, gas, light, etc., enters or escapes (Oxford Dictionary, 2007).

Thus oil contamination can be a result of oil spill or leakage.

2.1.1 Types of Oil Contamination

Oil contamination can be classified in different ways either in terms of part of environment that is contaminated or the location of the contamination. The classification is as illustrated in figure 2.1.

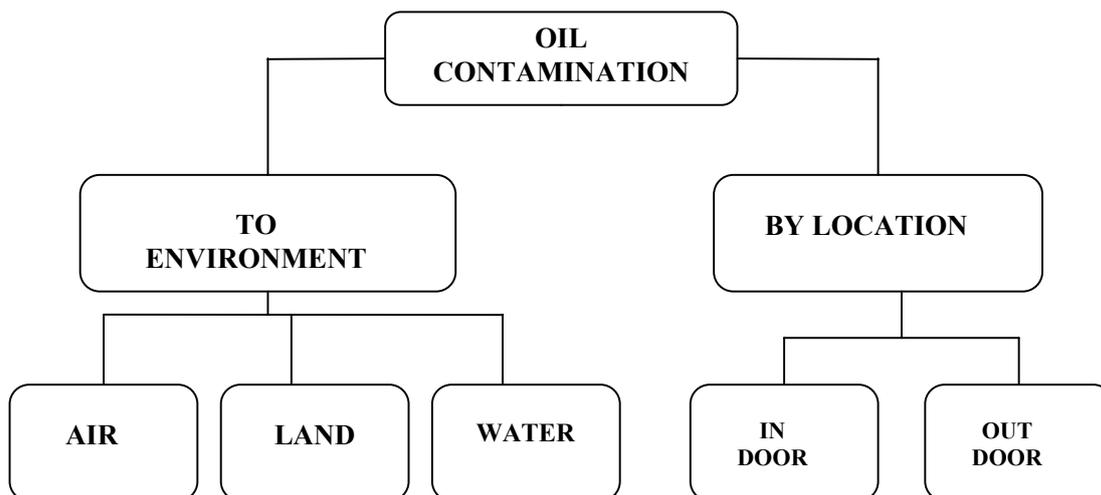


Figure 2.1: Classification of Oil Contamination

Oil Contamination of Environment

- *Oil Contamination of Air:*
According to National Safety Council; most oil fractions except gasoline do not contaminate air directly, rather by emissions coming from vaporization or release of VOC (volatile organic compounds), present in oil. The release can also occur during burning as fuel. Other means could be during the oil production and processing also as a result of spill or leakage (National Safety Council, 2006).
- *Oil Contamination of Land:*
Oil can be discharged directly on land. In this study land covers soil and wetland. The term contamination is most often used when the oil discharge is on land.
- *Oil Contamination of Water:*
This occurs when there is a discharge of oil on water or on water bodies. The term 'oil spill' is often used to describe such situation. An oil spill (sometimes called an oil slick) is the unintentional release of liquid petroleum hydrocarbon into the environment as a result of human activity. The term often refers to marine oil spills, where oil is released into the ocean or coastal waters (Wikipedia, 2007).

Oil Contamination by Location

- *Indoor Oil Contamination:*
This represents the situation where the oil spill occurred within an enclosure. This could be in garage from vehicle, walk ways, pipes, machines/engine, boats, from home heating oil storage tank (surface or underground storage tanks) etc. The spill could be as a result of accident, corrosion, mechanical damage, soil conditions or other factors.
- *Outdoor Oil Contamination:*
This is a situation where by the oil contamination /spill occurs outside an enclosure or outside a house. This could be on land or water. This also ranges from small scale spills in a surrounding compound, pools, pond or lakes to large scale spill in rivers and oceans.

2.2 Global Oil Spill

The International Tanker Owners Pollution Federation (ITOPF) has maintained a database of oil spills from tankers, combined carriers and barges since 1974. The database contains information on both the spill itself (amount and type of oil spilt, cause and location) and the vessel involved. It categorize spills by size (<7 tonnes, 7-700 tonnes and >700 tonnes) although the actual amount spilt is also recorded. Its data base contain information on about 10,000 incidents, of which 84% are small spills i.e. <7 tonnes. It stated that incidence of large spills is relatively low and detailed statistical analysis is

rarely possible but trends show a significant decrease in number of large spills (>700 tonnes) in the last thirty years (ITOPF, 2007).

Data on the number and amounts of small spills (less than 7 tonnes) is incomplete. More reliable data are held for spills, 7 tonnes and above. Information from ITOPF shows that majority of oil spill incidents occurred around Europe. Table 2.1 shows a summary of total oil spilt (7 tonnes and above) in decades from the 1970s to 2006.

Table 2.1: Total oil spilt (7 tonnes and above) in decades from the 1970s to 2006.
Source: ITOPF, 2007.

Decades	Quantity Spilt (tonnes)
1970s	3,142,000
1980s	1,176,000
1990s	1,138,000
2000-2006	176,000

2.2.1 Causes of Spill

Spills are usually as result of a combination of various actions and circumstance. For simplicity the causes of spill were grouped into operations (loading/discharging, bunkering, other operations) and accidents (collision, grounding, hull failures, fire & explosions) while spills in which there is no information about the cause are classified as other/unknown (ITOPF, 2007).

Figures 2.2, is a chart showing oil spill incidences and the percentage contribution of various cause factors for spills <7 tonnes up to year 2006. It shows that highest percentage (37%) of the cause for spills <7 tonnes is as a result of loading/discharging. From ITOPF, (2007) also found that for spills 7-700 tonnes loading/discharging is the main cause (causes 28%) of the spills. The situation is however different for spills >700 tonnes in which most of the cause is as a result of groundings and collision.

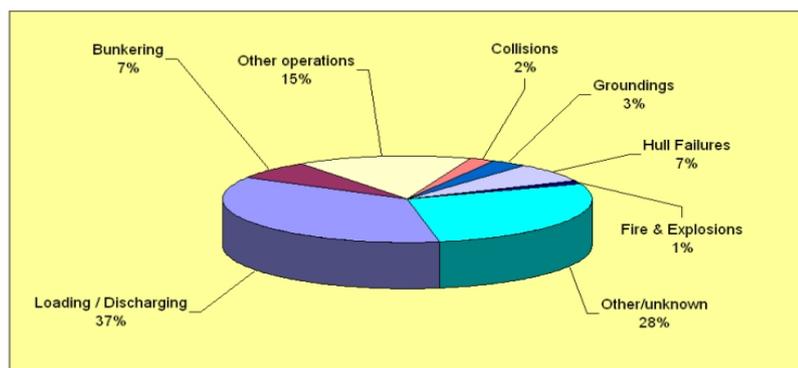


Figure 2.2: Spill Incidence <7 tonnes by Cause, 1974-2006. Source: ITOPF, 2007.

2.3 Oil Contamination in Sweden

2.3.1 Types of Oil Often Encountered

The following types of oil might be encountered in a spill decontaminating situation (Fejes, J., 2007);

- Indoor: non-mixed oil from machinery e.g. hydraulic oils, lubricants. mixed oil; oil mixed with detergents, emulsifiers or water (cutting oil/fluid)
- Outdoor: light product e.g. diesel, fuel oil 1, light crude oil (e.g. crude oil from north sea, Persian gulf, Russian crude etc.), kerosene , aviation fuel.

Equally encountered are all types of oil that are transported or used by ships. That is, a broad variety of different types of oil, e.g. bunker oil, crude oil, refined products (gasoline, kerosene etc), hydraulic oil, etc. (Schnell, A., 2007).

2.3.2 Volume of Spills

Information from McIntyre, C. (2007), states that the Swedish fire brigades are called out to about 2200 hazardous chemical spills each year. More than half of these are very small spills of petrol, diesel, motor oil or hydraulic fluid from road vehicles. It was noted that there is no figure available for oil only.

Volume of oil spills in Sweden varies according to location its location (Fejes, J., 2007);

- Indoors: few litres of oil are often involved. The cause is not usually accidental it is usually operational.
- Outdoor: 5-10m³ might be involved. Might be from leaks from oil tanker.
- Oil Spill to water: Up to 500-1000m³
- On sea is around 100-2000m³

The size of the spills dealt with in Sweden varies from less than a ton up to 10,000 tonnes (in a worst case scenario) or more (Schnell, A., 2007).

2.4 Types of Oil

For an efficient oil decontamination operation, the knowledge of the type of oil involved in the spill is mandatory, since the severity of an oil spill's impact depends on a variety of factors, including the physical properties of the oil, the type of oil, and the natural actions of the receiving waters on the oil. The decontamination method to use depends on the type of oil involved.

According to the United States Environmental Protection Agency (EPA), oils can be classified into petroleum based and non-petroleum based (EPA, 2006). Figure 2.3 gives an illustration of the various classes of oil.

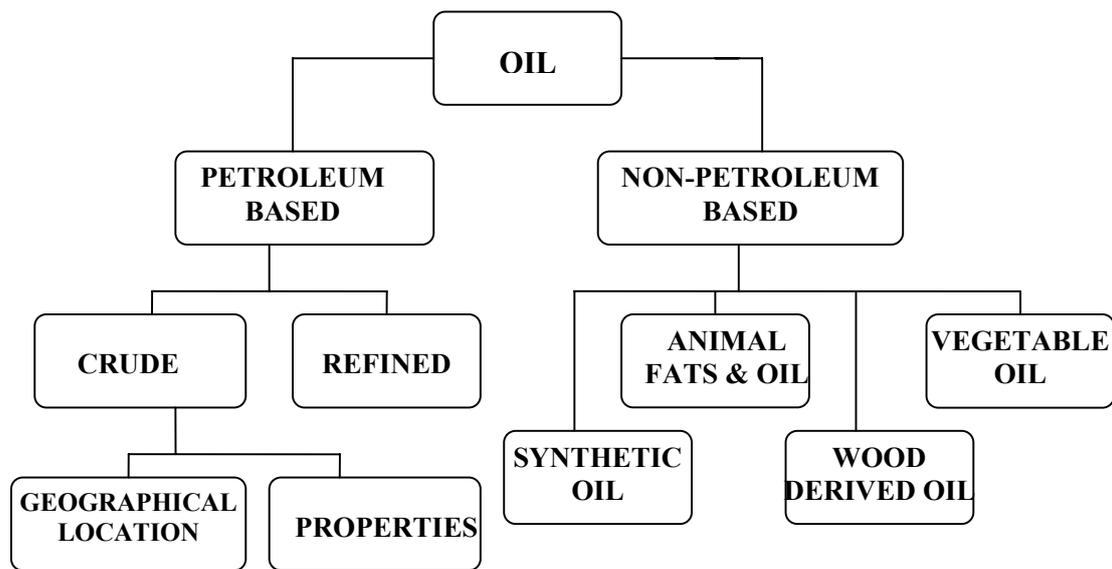


Figure 2.3: Oil Classification

2.4.1 Petroleum Based Oil

These are natural hydrocarbon based substances and refined petroleum products, each having a different chemical composition. They consist mostly of hydrocarbons in various molecular arrangements. Each type of crude oil and refined product has distinct physical properties that affect the way oil spreads and breaks down, the hazard it may pose to marine and human life, and the likelihood that it will pose a threat to natural and man-made resources. The rate at which an oil spill spreads determines its effect on the environment (EPA, 2006).

Types of Crude Oil

Crude oil can be classified either by their geographical location or according to their properties. Classification based on geographical source is generally not useful for decontamination purposes. Classification based on properties is more useful. The classification according to properties is as follows (EPA, 2006):

- *Class A: Light Volatile Oils.*
They are highly fluid, often clear, spread rapidly on solid or water surfaces, have a strong odor, a high evaporation rate, and are usually flammable. They penetrate porous surfaces such as dirt and sand. Most refined products and many of the highest quality light crudes can be included in this class.
- *Class B: Non-Sticky Oils.*
They have a waxy or oily feel. They are less toxic and adhere more firmly to surfaces than Class A oils. Their tendency to penetrate porous substrates increases with increase in temperature and they can be persistent

- *Class C: Heavy Sticky Oils.*
They are characteristically viscous, sticky or tarry, and brown or black. The oil does not readily penetrate porous surfaces. The density of Class C oils may be near that of water and they often sink. Toxicity is low.
This class includes residual fuel oils and medium to heavy crudes.
- *Class D: Nonfluid Oils.*
They are relatively non-toxic, do not penetrate porous substrates, and are usually black or dark brown in color. When heated, they may melt and coat surfaces making cleanup very difficult.
Residual oils, heavy crude oils, some high paraffin oils, and some weathered oils fall into this class.

For spilled oil, this classification can be dynamic because one class of oil can change to another depending on temperature and weather conditions e.g. Class B can change to Class C with decrease in temperature and vice versa.

Types of Refined Petroleum Products

These are products derived after processes such as fractional distillation or catalytic cracking of crude oil. Members in this type of oils are (EPA, 2006):

- *Gasoline:*
Lightweight, flows easily, spreads quickly, and may evaporate completely in a few hours under temperate conditions. It has high volatility and flammability thus poses a risk of fire and explosion. It is more toxic than crude oil. It is amenable to biodegradation. Use of dispersants is not recommended.
- *Kerosene:*
Lightweight, flows easily, spreads rapidly, and evaporates quickly. It disperses easily but is relatively persistent in the environment.
- *No.2 Fuel Oil:*
Lightweight, flows easily, spreads quickly, and is easily dispersed. This fuel oil is neither volatile nor likely to form emulsions, and is relatively non-persistent in the environment.
- *No.4 Fuel Oil:*
Medium weight, flows easily, and is easily dispersed if treated promptly. This fuel oil has a low volatility and moderate flash point, and is fairly persistent in the environment.
- *No.5 Fuel Oil (Bunker B):*
This is a medium to heavyweight oil with a low volatility and moderate flash point. Preheating may be necessary in cold climates. It is very difficult to disperse.

- *No.6 Fuel Oil (Bunker C):*
This is a heavyweight material. It is difficult to pump and requires preheating for use. It has a low volatility and moderate flash point. It may be heavier than water and is very difficult to disperse. It can form tar balls, lumps, and emulsions.
- *Lubricating Oil:*
It is medium weight, flows easily and is easily dispersed if treated promptly. This oil has a low volatility and moderate flash point, but is fairly persistent in the environment.

2.4.2 Non-Petroleum Based Oil

Many non-petroleum based oils have physical properties similar to petroleum based oils. Example, they have limited solubility in water, create slicks on the surface of water and form emulsions and sludges. They also produce similar environmental effect (EPA, 2006). Members in this category are (EPA, 2006):

- Synthetic oil such as silicone fluid, tung oil.
- Wood derived oil such as resin/rosin oil.
- Animal fat and oil.
- Vegetable oil:
 - ✓ edible seed oil from plant
 - ✓ inedible oil from plant

2.5 Oil Decontamination Methods

To decontaminate is to make free of contamination (Dictionary.com, 2007). Thus oil decontamination is cleaning to free oil from contaminated air, land or water. Oil decontamination process in the environment is commonly referred to as oil spill clean up or response.

International Petroleum Industry Environmental Conservation Association (IPIECA) stated that the aims of oil spill response are to minimize damage to environmental and socioeconomic resources, and to reduce the time for recovery of affected resources by achieving an acceptable standard of cleanliness (IPIECA, 2000). It noted that initiation of a response, or decision to stop cleaning or leave an area for natural clean-up, is based ideally on an evaluation which has taken place both before the spill (as part of the contingency planning process) and after the spill.

The decontamination of oil spill is a process that involves so many different techniques for minimizing their impacts on human health and the environment. The method to use depends on many factors, such a type of oil spill, the location of spill (land, water, sea, shoreline, rocky land, sandy beach etc), volume of spill, duration of spill, conditions at sea, water currents and wind.

Oil spill decontamination methods obtainable today can be classified into five different key categories. The categories of methods are as follows:

- Physical Methods
- Chemical Methods
- Biological Methods
- Natural Methods
- Thermal Method

2.5.1 Physical Methods

This involves all the oil decontamination techniques that involve a physical separation of oil spill from the contaminated environment. Techniques that can be found in this category include:

Containment and Recovery

Booms (or Oil Containment Booms)

Booms are floating devices that can be used for oil containment or recovery. When used for oil containment they have one or more of the following functions (Hvidbak, F., 2003):

- Deflecting oil to prevent oil slick from hitting sensitive areas.
- Containment of oil for later recovery by for instance a skimmer.
- Containment and concentration of oil for instant recovery by for instance a skimmer.

Figure 2.4 is an illustration of the use of boom for oil spill containment in the U configuration.



Figure 2.4: Towing Booms at Sea in U Configuration. Source: ITOPF, 2007.

Skimmers

A skimmer is a device for recovery of spilled oil from the water's surface. There are many types of skimmers but all are based on the simple principal: oil is lighter than water. Oil floats on the surface of water and thus if a way can be found to remove the top layer, oil can be collected easily (Exxon Valdez Oil Spill Clean Up Methods, 1993).

Sorbent Materials

Sorbents are insoluble materials or mixtures of materials used to recover liquids through the mechanism of absorption, or adsorption, or both. Absorbents (use the principle of

absorption) are materials that pick up and retain liquid distributed throughout its *molecular structure* causing the solid to swell (50 percent or more). Adsorbents (use the principle of adsorption) are insoluble materials that are coated by a liquid on its surface, including pores and capillaries, without the solid swelling more than 50 percent in excess liquid (EPA, 2006).

To be useful in oil decontamination, sorbents need to be both oleophilic (oil-attracting) and hydrophobic (water-repellent). They can be used as the sole cleanup method in small spills, but are most often used to remove final traces of oil, or in areas that cannot be reached by skimmers. Figure 2.5 is an illustration of the use sorbents in oil decontamination.



Figure 2.5: Use of Sorbent Materials for Oil Spill Decontamination
(Source: EPA Oil Program; Photo Gallery, February 3rd, 2007)

Sorbents can be: natural (organic or inorganic) or synthetic (EPA, 2006).

Natural Organic Sorbents: include peat moss, straw, hay, sawdust, ground corncobs, feathers, and other readily available carbon-based products. They can adsorb between 3 and 15 times their weight in oil.

Natural Inorganic Sorbents: Examples in this category are; clay, perlite, vermiculite, glass wool, sand, or volcanic ash. These can adsorb from 4 to 20 times their weight in oil. These types of sorbents are not used on the water's surface.

Synthetic Sorbents: These are man-made materials. They can either *adsorb* liquids onto their surfaces (like a sponge); examples polyurethane, polyethylene, and polypropylene (mostly linear and branched polymers) or *absorb* liquids into their solid structure, causing the sorbent material to swell, examples include cross-linked polymers and rubber materials. Synthetic sorbent that cannot be cleaned after use can pose a problem because they must be stored temporarily before proper disposal.

Hydraulic Measures

This is mostly applicable in shoreline clean-up (ITOPF, 2007). In general the following hydraulic measures can be applied: Flooding, Low Pressure Water Washing and High Pressure Hot Water Washing. Figure 2.6 shows the use of high pressure; hot water washing technique in shoreline clean-up.



Figure 2.6: High Pressure, Hot Water Washing in Shoreline Clean Up
(Source: Exxon Valdez Oil Spill Clean Up Methods, 1993)

Mechanical Treatment

This method involves the use of Bulldozer to expose the oil when it has penetrated several inches into the soil so that it can be removed from the site or left to degrade naturally.

Manual Removal

Rakes and shovels can be used to remove bulk oil manually from hard-packed sand beaches. This usually involves a team of well-organized laborers

2.5.2 Chemical Methods

These techniques involves all methods that involve the use chemicals to modify the oil contaminants in order to aid it removal or absorption into the environment. Methods in this category include:

Dispersants

These are group of chemicals designed to be sprayed onto oil slicks, to accelerate the process of natural dispersion (ITOPF, 2007). They are chemicals that contain surfactants and/or solvent compounds that act to break petroleum oil into small droplets. Dispersants act by altering the balance between natural dispersion (oil droplets in water) and

emulsification (water-in-oil droplet) by pushing the balance towards dispersion away from emulsification (IPIECA, 2001). Chemicals that act in this way are sometimes known as Demulsifiers (Zhu, X., et al., 2001). Figure 2.7 shows dispersing agents in action.

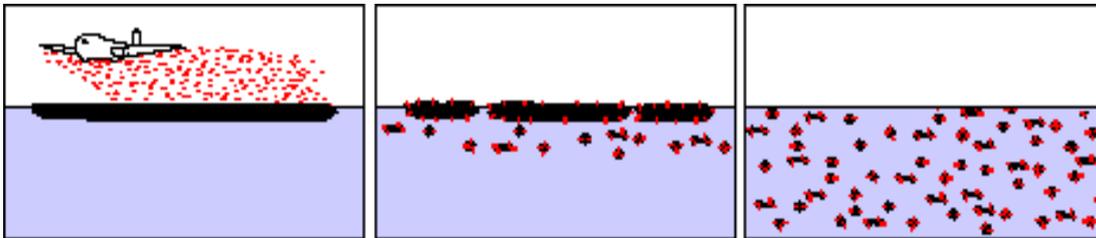


Figure 2.7: Dispersing Agents Aerial Spraying and Action.

Source: ITOPF, 2007.

Gelling Agents (Solidifiers)

These are chemicals that react with oil to form rubber-like solids. They can be applied by hand (in small spills) then allowed to mix on their own but in large spill they are applied and then mixed using high-pressure water streams (EPA, 2006).

Surface Film Chemicals

These are film-forming agents used to prevent oil from adhering to shoreline substrate and to enhance the removal of oil adhering to surfaces in pressure washing operations (Zhu, X., et al., 2001)

2.5.3 Biological Methods

This involves the use of biological agents (chemicals or organisms that increase the rate of natural biodegradation). Biodegradation is a process by which microorganisms such as bacteria, fungi, and yeast break down complex compounds into simpler products to obtain energy and nutrients (EPA, 2006). Biodegradation of oil is a natural process that slowly removes oil from the environment; this can take years.

Bioremediation

Bioremediation is the addition of materials to contaminated environments to accelerate the process of natural degradation (Zhu, X. et al., 2001). It noted that there are two approaches to bioremediation:

Bioaugmentation (Seeding): the addition of known oil-degrading bacteria to supplement the existing population.

Biostimulation (Fertilization): the stimulation of growth of natural oil degraders by addition of nutrients. This is often called nutrient enrichment.

Phytoremediation

This is the use of plants and their associated microorganisms for remediation. It is a low cost process and is proving effective for a wide variety of contaminants including petroleum and hydrocarbons (Fingas, M. and Charles, J., 2001). This method takes years to remediate a site and clean up is limited to the depth of soil within the reach of plants' roots.

2.5.4 Natural Methods

This is allowing nature to clean up the spill through natural processes at its own pace. These methods usually take long time. But for some spills, this is the cost-effective and ecologically sound method (Fingas, M. and Charles, J., 2001).

Key natural processes that result to oil degradation are: evaporation, biodegradation, photooxidation (the reaction of oxygen with oil compounds in the presence of sunlight resulting to oil breakdown).

2.5.5 Thermal Method

In-Situ Burning

Burning oil is a very effective way of reducing the amount of oil on the water. When a burn is conducted, tens of thousands of gallons of oil can be reduced into tarry residue. This residue is then easily recovered by hand or scooping devices. However, this method has a lot of environmental concern.

In generally, effective oil decontamination usually involves a combination of these methods.

2.6 Oil Combating In Sweden

Outdoor oil contamination often occur on shorelines and land in Sweden (Schnell, A., 2007) and (Källström, H., 2007). Most common operation where oil spill occur are in harbors. Operations here are commonly bunkering and loading of oil such as diesel, fuel oil 1. Most frequently about 100-200 litres or less is involved (Fejes, J., 2007).

In combating the oil spill, pumps and skimmers are used if possible. In addition to that: mechanical (front loaders etc), manual (shovels or similar, hand tools), flushing, sorbents (Zugol, Ecobark) are equally used (Schnell, A., 2007). Källström, H., 2007; mentioned that mechanical and manual methods are used in oil combating. Small spills are dealt with by spreading an absorbing material (such as Absol) which soaks up most of the liquid (McIntyre, C. 2007; Fejes, J., 2007).

Figures from Swedish Rescue Service Agency in 2006 for all chemical spill decontamination (there is no figures available for oil only) show that the following methods were used (McIntyre, C. 2007):

- Absorption - 1294
- Sealing drains - 94
- Damming - 178
- Booms on river - 79
- Digging up contaminated soil - 63

It equally stated that large spills are contained by sealing drains, damming small ditches and using booms to stop the spread of oil on rivers. Contaminated soil will later have to be removed.

2.7 Oil Combating Actors in Sweden

The responsibility for the Swedish environmental rescue service in the event of oil spill is shared between several national, regional and local authorities (Swedish Rescue Service Agency, 2005). These include:

The Swedish Rescue Service Agency: coordinates the public sector activities within the rescue services and supervises the municipal fire brigades. If necessary it supports the municipal authorities with personnel and materials from the five regional oil combating depots. It participates in the working party of the Helsinki Commission (HELCOM) on issues concerning combating pollution, EU Management Committee on Marine Pollution, Copenhagen Agreement and the Arctic Council.

The Swedish Coast Guard: is responsible for emergency services when oil or other hazardous chemicals have leaked into water. Its task also includes monitoring the adherence to national and international regulation on protection of the environment. Coast Guard is Sweden's representative in the working party of the Helsinki Commission (HELCOM) on issues concerning combating pollution, EU Management Committee on Marine Pollution, the Bonn Agreement, Copenhagen Agreement and the Arctic Council.

The Swedish Maritime Administration: is responsible for measures aimed at preventing oil emissions from vessels and emergencies at sea. It is Sweden representative in the HELCOM in working party on maritime issues, as well as in the UN's international Maritime Organization and in the EU's maritime safety partnership.

The Swedish Environmental Protection Agency: is the national environmental authority; its task includes monitoring the environmental effects of oil spills.

IVL Environmental Research Institute: has agreement with the Environmental Protection Agency which involves maintaining an 'emergency oil service' in the institute from which municipal authorities can obtain advice about oil decontamination. Emergency oil service assist in providing expert support to the Environmental Protection Agency and other authorities in the event of oil spill in the sea and in inland water ways.

Municipal Authorities: in addition to the Civil Protection Act are also responsible for fire and rescue services within their own areas. Oil that threatens come ashore is will

normally be regarded as ground to call in fire and rescue service and if the oil has already come ashore that intervention required is decontamination.

2.8 Absorbents for Oil Spill Decontamination

In section 2.5.1 a brief introduction was given about sorbents. In this section effort will be channeled towards a more detailed discussion on the use of absorbents for oil decontamination purpose.

2.8.1 Sorbents

Oil sorbents are wide range of products used to soak up oil in preference to water. They are most appropriately used during the final polishing stages of clean-up and for recovering small pools of oil inappropriate for other techniques (ITOPF, 2006). Disposal of oiled sorbent material can contribute significantly to the overall decontamination cost.

As mentioned earlier we have natural (organic and inorganic) and synthetic sorbents. Sorbents can also be classified as either *absorbent* or *adsorbent* material.

This study is focused on the use of absorbent material (tyre granulate) for oil decontamination.

2.8.2 Absorbent Materials

Absorbent materials are mostly synthetic materials. They are materials that act by the principle of absorption in which liquid is incorporated into the body or pores of a material causing the material to swell. Absorbents combine with oil in such a way that it cannot leak or be squeezed out. Only few sorbents are true absorbents (ITOPF, 2006).

Examples include; cross-linked polymers such as (vulcanized) rubber materials.

Some sorbents can be cleaned and reused several times. Synthetic sorbent that cannot be cleaned after use can pose a problem because they must be stored temporarily before proper disposal (EPA, 2006). Disposal of oiled sorbent material can contribute significantly to the overall decontamination cost.

2.8.3 Absorbent Forms

Absorbents are marketed in various shapes and forms depending on their composition and intended use. Three main categories have been identified (ITOPF, 2006):

Absorbents in Bags

They are loose particulate absorbent packaged in bags. They are usually in the form of granules. Figure 2.8 is a picture of absorbent packaged in bags.



Figure 2.8: Absorbent in Bags. Source: Andax Industries L.L.C, USA.

Enclosed Absorbents

The absorbent materials are enclosed with either fabric, mesh or netting in order to enhance their ease of use. The forms found in this category include: Booms, Pillows or Socks. They only vary by their shapes and volume. Figure 2.9 gives illustration of pillows and socks.

Boom is the most widely used of these configurations.



Figure 2.9: Absorbent Pillows and Socks. Source: ExtremeGB Ltd., United Kingdom.

Continuous Absorbents

Absorbent materials in this case are made into continuous forms in which their length and width are much greater than their thickness.

Examples are: absorbent sheets, pads, rolls, blanket, mats, rugs, webs and sweeps. Booms are also constructed using continuous materials.

Illustrations of sorbent booms and mat are shown in figure 2.10 while figure 2.11 shows sorbent pads and roll.

Loose Fibre Sorbent

Sorbents in this form are useful in recovery of more viscous oil. They are usually produced from stripes of polypropylene made in form of ‘pom-poms’ which are often combined using a rope to form viscous oil sweeps called ‘snare boom’. Sorbent pom-poms and the use of sorbent blanket are shown in figure 2.12.



Figure 2.10: Sorbent Boom and Mat. Source: Andax Industries L.L.C, USA.



Figure 2.11: Sorbent Pad and Roll. Source: Andax Industries L.L.C, USA.



Figure 2.12: Sorbent Pom – Poms (Source: Spill911, USA) **and Sweep** (Source: Andax Industries L.L.C, USA)

2.8.4 Properties of Absorbents

The following are the desirable properties of absorbents (sorbents) (ITOPF, 2006):

Buoyancy	A good absorbent must remain afloat when saturated with oil if it to be used effectively in decontamination of marine environment, particularly when the oil is less viscous.
Saturation	Sorbents should be able to reach quickly so as to make oil decontamination operation fast and more efficient.
Strength and Durability	Sorbents should be strong and durable since they may be left for sometime on site.
Wettability	For a material to be a good absorber, it must have to be oil attracting (oleophilic) and water repelling (hydrophobic). For a liquid to wet a solid, its surface tension must be less than the critical surface tension (γ_C) of the solid. Many natural and synthetic solids have suitable γ_C value.
Capillary Action	Uptake of oil by absorbents is usually via capillary action (Bertrand P.A., 1993). Absorbents work by drawing liquid into the molecular structure of the material (ITOPF, 2006). Capillary action depends on relative surface tension of the solid and liquid but is mostly affected by the viscosity of the oil. Less viscous oil (e.g. No. 2 Fuel Oil) penetrates very fast when compared to highly viscous oil (e.g. Bunker C). Absorbents are more suitable for less viscous oil (ITOPF, 2006).
Surface Area	The surface area of a sorbent is directly proportional to its sorption rate.
Cohesive Properties	This property opposes the spreading of liquid on a surface. This property is usually an advantage for the sorption of heavy oil. Cohesion is greater with more viscous oil.

2.8.5 Factors to Consider in the Choice of Absorbent

In choosing the absorbent to use for oil decontamination, the following should be considered (EPA, 2006) and (ITOPF, 2006).

Absorption Rate	Oil absorption is faster with lighter oil products. Oil cannot be released once absorbed. It is more effective with light hydrocarbons like gasoline, diesel fuel, benzene etc.
Adsorption Rate	Thicker oils readily adhere to the surface of adsorbents.
Oil Retention	This is the ability of the absorbent to withhold the absorbed oil without losing it when lifted from contaminated site. Leaching causes secondary contamination, however, absorbent materials are not prone to leaching.

Ease of Application	Sorbents may be applied to contaminated sites manually or mechanically, using blowers or fans. This however depends on the form of the absorbent.
Cost	Natural sorbents are generally cheaper than synthetic ones, but their low efficiency and the consequent higher volume purchase is worth considering. Synthetic sorbents are more expensive but are more efficient and can also be reused.
Dispersants Effect	Use of dispersants and other spill response chemicals can negatively affect the use of sorbents since these chemicals act by altering the surface tension of both oil and water. This thus decreases the oleophilic and hydrophobic properties of the sorbents.
Availability	Effective sorbents should be readily available for clean-up operations.
Transportation	Transport of large amount of sorbent materials from warehouse to spill location can create logistic problems. Although the sorbent materials are not heavy, they can be bulky.
Recovery	Sorbents will become pollutants unless they are recovered from the spill site.
Storage	Two types of storage should be considered; <ul style="list-style-type: none"> • <i>Stockpiles</i>: Sorbent materials are bulky thus require more storage space when compared to other form of response equipment or material. Consideration should be given to flammability of the material. • <i>Oiled material</i>: Recovered sorbent materials have larger volume than the oil or sorbent alone. Also piling of oiled material should be in an enclosure to prevent recontamination from leaching.

2.9 Use of Absorbents

Absorbents can generally be used in both indoor and outdoor oil decontamination exercise.

2.9.1 Indoor

This is a situation whereby an absorbent is used for spill decontamination within an enclosure. This can be at home, office, industry, recreation site, in vehicles, boat, ship etc. Figure 2.13 gives illustrations of the some indoor use of absorbents in our daily activities.



Figure 2.13: Absorbents in Action in Daily Activities
 Source: Allmaritim AS, Norway.

2.9.2 Outdoor

This is the situation where absorbents are used outside an enclosure for oil decontamination exercise. This can be on land, shore or water.

Absorbent Use On- and Near-Shore

Sorbents can be used on shore for example in situations where it is difficult to handle fluid oil, to recover sheen and thin films of oil that is difficult to recover etc. However as mentioned earlier factors such as storage, transport, availability etc. should also be considered in any situation.

Absorbent Use at Sea

The use of absorbents (in forms that will affect natural evaporation of oil) on the sea as the primary response tool in major spill response is not advocated. This is because the sorbents inhibit the natural evaporation and dispersion of certain oils which are the processes that would help in their rapid removal from the sea surface.

2.10 Disposal of Absorbents

The following disposal options can be considered for the oiled absorbent material:

Reuse

Oil trapped in the sorbent material can be extracted and the material re-used. The following methods can be used for extraction:

- Compression (using mangle or wringer): more suitable for synthetic materials especially foam based sorbents. Figure 2.14 is an illustration of the use of wringer for extracting oil from sorbents meant for re-use.
- Thermal regeneration by water vapor, hot air or vacuum vapor is also possible.
- Centrifuge
- Solvent extraction.

Factors to be considered when using this method include:

- Number of cycles materials can be reused due to deterioration from tearing and crushing.
- Decrease in sorption capacity and amount of oil that can be removed. Sorption capacity of some sorbents however tend to increase with repeated reuse for viscous oils.
- Contamination of recovered waste oil by particulates from the sorbent.



Figure 2.14: Absorbent Hand Wringer for Extracting Oil for Sorbent Re-Use
Source: Global Spill Control, Australia.

It should be noted that release of oil from absorbent polymeric materials is not possible by squeezing. They can be depolymerized at elevated temperatures to release the oil while recovering the materials in different form.

Recycling

If oil residue has been removed properly and material is not damaged, sorbent materials can be recycled and marketed. Further research is however required in this aspect.

Biodegradation

This is generally applicable to organic sorbents since they are biodegradable. They can be disposed of by landfarming in which the oil materials are spread out over a land area. Degradation can take number of years however this can be shortened by aeration and fertilization. Composting is also possible.

Incineration

The incineration of sorbent material is a disposal method as well as a valuable source for energy due to their high calorific value as a result of the absorbed oil. Synthetic sorbents has high calorific value thus necessitates adequate control of the kiln or furnace and feed rate during combustion.

Also control and strict monitoring of exhaust gas is necessary due to the possible production of dioxins, PAH, HCl.

Landfill

This is not an option in some countries example Sweden where landfilling of waste has been prohibited.

In countries where landfills are acceptable, compression of disposed sorbent can result in leaching thus site should be enclosed with impermeable membrane to prevent run off.

2.11 Discussions on Oil Decontamination

For oil decontamination to take place, there must be contamination. Oil contamination can be classified into contamination to environment in which we have air, land and water or contamination by location in which we refer to indoor and out door contaminations.

ITOPF data base of oil spill incidents since 1974 in which it classified spill incidents into three categories; < 7 tonnes, 7-700 tonnes and >700 tonnes has shown that vast majority of spills (84% of 10,000 incidents) fall into the smallest category (<7 tonnes).

In Sweden, about 2200 hazardous chemical spills occur each year; most of these are small spills of petrol, diesel, motor oil or hydraulic fluid from road vehicles. Globally, the incidents of large spills are low.

Various factors contribute to oil contamination. These can simply be grouped into accidents, operations and others. Spills incidents of <7 tonnes and 7-700 tonnes are mostly as a result of operations while large scale incidents >700 tonnes are mostly due to

accidents. Oil contaminations in Sweden often occur on shorelines and land; the most common operation that results to oil contamination here are due to bunkering and loading of oil in the harbors.

Type of oil is one of the key factors in determination of the decontamination method to use in a response operation. Two major classification of oil are petroleum based and non-petroleum based oils. Petroleum based oil is further divided into crude oil and refined petroleum products. Crude oil can be classified either based on geographical source or based on its properties. Classification based on properties is useful for response purpose. Generally, petroleum and non-petroleum based oils share similar physical properties and produce similar environmental effects.

Oil decontamination is the process of removing oil contaminants from the environment in order to reduce the impact on plant and animal life. Decisions on the mode of oil decontamination should be part of a contingency planning process.

Several methods are available for an oil decontamination exercise. These can be classified into Physical, Chemical, Biological, Natural and Thermal methods. Each of these methods has their inherent disadvantage. The use of any method depends on many factors such as the type of oil to decontaminate the location of the spill, the prevailing environmental conditions. For instance in water, factors such as wind, current or sea state play crucial role in determination of the method to use.

Physical methods of recovery and containment (booms, skimmer and sorbents) are widely used with booms being the most widely used in open sea operations. These methods are also effective especially in calm water conditions. In rough waters their efficiency is highly reduced since the oil spreads fast and will be difficult to contain and recover. Sorbents can be used as the sole cleanup method in small spills, but are mostly used to remove final traces of oil and in areas that cannot be reached by skimmers.

Hydraulic measures are useful on the shoreline but are of concern when high pressures are used because of its aggressiveness to the natural habitat. Mechanical and manual removals are used when the oil has penetrated or strongly stocked into the soil. These techniques however can deform the face of the beaches or land.

In chemical methods, dispersants are used to disperse the oil in order to accelerate the rate of natural dispersion, but this is more effective for less viscous oils since high viscous oils do not disperse easily. Biological methods use additional or stimulated microorganisms and plants to convert the oil into carbon dioxide, water and biomass. This method takes longer time and is more adequate at the final clean up stages. Natural method allows nature to take its course and this takes time. Thermal method is in-situ burning operation it removes the oil very fast but has a lot of environmental consequences. In general, no single method is the most effective. A combination of methods will be more practical.

The most common methods used in oil combating in Sweden are physical methods especially absorbents since mostly small spills occur. Commonly used absorbents are Absol, Zugol and Ecobark.

Oil sorbents are materials that soak up oil in preference to water. In order to be a good sorbent for oil, the material should be hydrophobic (water-repelling) and/or oleophilic (oil-attracting). They work by mechanisms of absorption or adsorption or both. Materials that soak oil by *absorption* mechanism are known as *absorbents* while materials that work by *adsorption* mechanism are known as *adsorbents*. Sorbents on the other hand refers to either of the two materials. Sorbents can be natural (organic and inorganic) or synthetic.

Natural organic adsorbents include: bark, peat moss, saw-dust, paper-pulp, cork, chicken feathers, straw, wool, hay, ground corncobs, and other readily available carbon-based products. Natural inorganics adsorbents include vermiculite, pumice, clay, perlite, glass wool, sand, or volcanic ash. Synthetic sorbents are man made and can either adsorb liquid onto their surface (examples polyurethane, polyethylene, and polypropylene), they are mostly linear and branched polymers or absorb liquids into their solid structure, causing the sorbent material to swell, examples include cross-linked polymers and rubber materials.

Absorbents combine with oil in such a way that it cannot leak or be squeezed out thus attention have to be paid to its disposal after use since it cannot be cleaned for reuse. Only few sorbents are true absorbents.

Absorbents are marketed in various forms and sizes. This can be classified into Absorbents in Bags in which the absorbents are in form of particulates or granules packed in bags. Other forms are Enclosed Absorbents in which the absorbent materials are enclosed with either fabric, mesh or netting in order to enhance their ease of use, examples of this form of absorbents are Booms, Pillows, Socks. Continuous Absorbents in which the absorbent material is made in continuous form with their length and width much greater than their thickness, examples are absorbent sheets, pads, rolls, blanket, mats, rugs, webs, sweeps and booms. They are mostly made from synthetic materials especially polypropylene. Loose Fibre Sorbent are usually in the form of 'pom-poms' usually made from polypropylene and are useful in viscous oil recovery.

Certain properties are desired from a good absorbent, these include buoyancy, should be able to keep afloat after saturation; strength and durability since they may be left for sometime on site; wettability, it must be oil attracting (oleophilic) and water repelling (hydrophobic); capillary action, fast uptake of oil; surface area, is proportional to absorption rate; cohesive properties, the greater the cohesive effect on the oil the less the spread hence the easier to decontaminate.

In choosing the type of absorbent to use for a decontamination exercise certain factors need to be considered such factors are the absorbents absorption and adsorption rates, oil retention capacity, ease of application, availability, transport, storage, recovery, effect of dispersants and cost.

After use absorbents can create additional problems if not properly disposed since they will be voluminous and heavy after being oiled. Reuse with oil recovery, recycling incineration, and biodegradation are worth considering as disposal options and in accordance with country, state and local legislations.

Findings from this study have shown that absorbents are more useful during the decontamination of small spills. Absorbent therefore can be seen as an important decontamination method since majority of oil spills both globally and within Sweden are small spills. Further study on development of absorbents for oil decontamination using tyre rubber granules will be a welcomed innovation since this will be solving the oil spill and tyre problems simultaneously.

3. TYRE GRANULATE AS AN OIL ABSORBENT

Tyre granulate is the product derived from granulation of end-of- life tyres. Tyre granulation is the mechanical shearing of tyre to reduce it in size into finely dispersed particles of under approximately 10mm, from which metals and textiles and extraneous debris are removed (Basel Convention, 1999).

Tyre granulation can be by two principal methods (ETRA, 2007):

Ambient Size Reduction: Involving use of mechanical processes at or above ordinary room temperature to reduce the tyre to desired sizes. It produces granulate of 2-10mm.

Cryogenic Size Reduction: This uses liquid nitrogen or commercial refrigerants to embrittle the rubber to reduce it to desired size. It produces granulate of 0.5-2mm.

The following are the final products derived after tyre granulation (Genan, 2004):

- Rubber powder and granulate, 66%
- Steel, 20%
- Textile, 12%

The remaining 2% is waste.

Bulk specific gravity and porosity of rubber granules were measured using standard methods; APHA-AWWA-WPCF, 1989. The surface area was measured by nitrogen adsorption method (BET 624, Micro-meritics, Germany). Scanning Electron Microscope studies of waste tyre rubber granules were carried out using SEM (LEO S-440, German). It showed the presence of iron compounds, zinc, silica etc. in the rubber granules samples. Zn content was measured by atomic absorption spectrophotometer (AAS 670, Shimazu, Japan). Thermo Gravimetric Analysis (TGA) was conducted for chemical analysis of waste tyre rubber granules using TGA (DT-40, Shimazu, Japan) (Alam, J. B. et al., 2006). The physical and chemical characteristics of waste tyre rubber granules as determined by above tests are described in Table 3.1 below:

Table 3.1: Physical and chemical characteristics of waste tyre rubber granules

Parameters	Values
Bulk specific gravity	0.284 g/cm ³
Porosity	0.12-0.14
Surface area	0.45-0.78 gm/m ²
Carbon black	48-52%*
Polymer matrix	30-33%*
Other materials	Silica, Zinc oxide, Iron etc.**
Ash content	2-3%

As determined by * TGA test, ** SEM test.

Source: Alam, J. B. et al., 2006.

Tyre granulate is derived from tyre which is composed of different chemical substances. Therefore before tyre granulate can be used in any product development, it is important

to assess the properties of granulate with respect to the intended application. It is also necessary to assess the properties of granulate with respect to its impact on health and environment.

It is important that any product being developed should not only be suitable for the application but should also be safe to health and environment.

In this section of the report properties of tyre granulate were reviewed with focus on the absorption as well as environmental properties of tyre granulate.

3.1 Absorption Properties of Tyre Rubber Granulate

The process of manufacturing tyres combines raw materials into a special form that yields unique properties such as strength, resilience, and high absorbance of chemicals (Edil & Bosscher, 1994). Rubber from scrap tyres has been reported to absorb four to five times its weight of oil (Prudnikov and Smtanjuk, 1994; Perry and Chillton, 1983).

Aisien, F. A. et al, (2002) investigated the potential of using rubber recycled from scrap tyres as an absorbent in crude oil clean up. Rubber particles of mesh sizes within the range of 0.15 to 2.36 mm were used to absorb crude oil at different temperatures (5 to 40 °C). Figure 3.1 is a plot of the variation of absorption at 30°C (303K) with rubber particle sizes in the presence of crude oil obtained from the experiments.

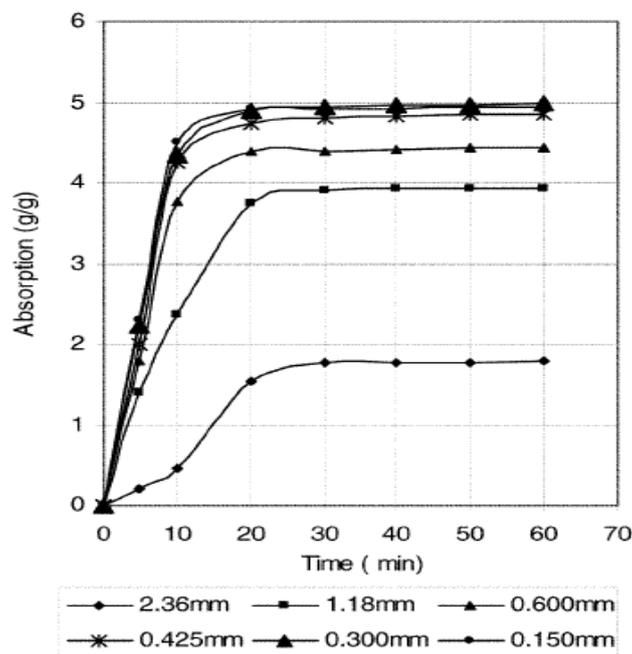


Figure 3.1: Variation of absorption at 30°C (303K) with rubber particle sizes (crude oil only). Source: Aisien, F. A. et al, 2002.

The plot shows a rapid increase in oil absorption within the first 20 min was followed by a much slower rate, with the equilibrium absorption being attained after 30 min. The equilibrium absorption increased with decreasing particle size and decreasing

temperature of absorption. At 30 °C, the oil absorption for the 0.15 mm rubber particles was more than twice that of the 2.36 mm particle size. When regenerated recycled rubber was used, the equilibrium absorption decreased by about 15–40%. The extent of reduction was higher for the larger particles and at lower temperature of absorption.

The report concluded that scrap tyre granulate has demonstrated the potential for use in oil spill clean up, because of its intrinsic ability to absorb oil. It went further to state that the presence of water does not have a significant influence on the extent of oil absorption by recycled rubber, this implies that tyre granulates can be used for oil decontamination in open seas, rivers and creeks. The report also concluded that regenerated recycled rubber is less efficient than fresh recycled rubber in potential oil clean up.

Sorption capacity of organic compounds by tyre granulate, was investigated using only granulate tyre rubber not tyre chips; thus it was possible to identify which part of tyre chips that played a major role in sorbing organic compound. It was found that organic compounds sorbed primarily onto tyre rubber polymeric materials and partially other materials in tyre rubber such as carbon black (Kim et al., 1997).

Synthetic rubber is one of the major components of car tyres (Rubber Manufacturers Association (RMA), 2007). Styrene butadiene rubber (SBR) on the other hand is a major component of synthetic rubber found in tyres. Table 3.2 shows the composition of the synthetic rubber component of an average European car tyre.

Table 3.2: Composition of Synthetic Rubber Component of an Average European Car Tyre. Source: BLIC (Bureau de Liaison des Industries du Caoutchouc), 2001.

Rubber Type	Estimated Share in Synthetic Rubber, %
Styrene-Butadiene Rubber(SBR)	74-81
Polybutadiene, butadiene, isoprene	15-21
Halogenated copolymers	3-4
Chlorobutyl rubber	1

Non polar organic compounds such as benzene, toluene, trichloroethylene, and tetrachloroethylene, are attracted by non polar materials such as SBR (Edil, T. B., 2007). Overall, tyre granules show significant capacity as a sorbent of organic compounds.

It has been found that tyre chips have 1.4 to 5.6% of the sorption capacity of granular activated carbon on a volume basis. Also when organic compounds are sorbed in tyre chips, only 3.5 to 7.9% were desorbed. Tyre chips have relatively high volatile organic compounds (VOCs) sorption capacities based on batch isotherm tests on scrap tyre chips. This suggests yet another innovative environmental application in which shredded tyre chips could be used to eliminate VOCs from contaminated water or leachate thus alleviating the contamination problems (Park, et al., 1996).

Twin City Testing Corporation (TCTC) indicated that the average concentrations of zinc, iron, and manganese increased in the groundwater samples under a tyre stockpile but at the same time the concentration of petroleum hydrocarbons decreased from 11.8 to < 0.5 mg/L compared to background groundwater samples indicating the potential of tyres to

absorb petroleum hydrocarbons. Therefore, another application for scrap tyres is to use them as a sorptive medium taking advantage of their sorptive quality to chemicals (TCTC, 1990).

Scrap tyre chips were used to demonstrate the effect of tyre chips on leachate from landfill. The method was applied based on batch isotherm tests, which showed scrap tyre chips to be good sorbents of VOCs and could be used as leachate drainage layer material in solid waste landfills and in other similar applications, both laboratory and field tests were conducted. The laboratory test showed the ability of tyre chips to absorb VOC's such as methylene chloride, toluene, and trichloroethylene. Also the field test in which two test cells of landfill were spiked with gasoline, it showed that concentrations of VOC's in the leachate was lowered significantly this is due to the sorptive characteristics of tyre chips (Edil, T.B. et al., 2004). In another study to investigate the performance of tyre chips as leachate collection material in municipal solid waste landfills, it was found that the leachate collected from the tyre-chip layer had lower inorganic compound, dissolved metal and VOC concentrations than those collected from the gravel layer (Aydilek et al., 2006).

In the publication, Suitability of shredded tyres as a substitute for a landfill leachate collection medium; result from leachate test after 800 days showed the ability of tyre chips to absorb certain metals such as arsenic, selenium, mercury, barium, and lead but not zinc. Also the field test showed the sorptive abilities of tyre chips on metals such as Arsenic, cobalt, lead, and nickel but not chromium, copper, iron, and molybdenum. It also stated that oil and grease levels were significantly lower in the tyre chip-containing cell than the gravel-containing cell probably due to sorption to tyre-chips.

It stated that, despite the concern with potential leaching of organic and inorganic contaminants, if tyre-chips are used in areas where contamination levels are high, then they can be used as a cheap sorbent for environmental clean-up (Park, J. K. et al., 2003).

The performance of a fixed-bed adsorber (FBR) column for the removal of anionic surfactants from aquatic environments has been studied. Waste tyre rubber granules were used as the adsorbent material, and sodium dodecyl sulfate, an anionic surfactant, as the adsorbate. The bed efficiency obtained for the removal of anionic surfactants by waste tyre rubber granules was 90.97% (Purakayastha, P. D. et al., 2003).

3.2 Environmental Properties of Tyre Rubber Granulate

A better understanding of the interaction between tyre granulate and the environment is essential for the development of innovative uses of tyre rubber granules. To comprehensively study the environmental properties of tyre granulate, a review of the leaching, emission and ecotoxicological properties as well as potential impact on health is given.

3.2.1 Leaching Properties

To leach is to remove (a soluble substance) from soil or other material by the action of rainwater or another liquid passing through it (Oxford Dictionary, 2007). Leaching of

substances from granulate is very important to consider since some of the materials used in tyre manufacture today has been identified as hazardous, thus are not desirable to be released to our environment (at quantities beyond acceptable limits) during handling of the granulate or use of the granulate derived products.

Factors Affecting Tyre Granulate Leaching

The main factors affecting the characteristics of leachates from tyre chips include the aquatic environment in which the tyre chips are exposed, the age of the tyres, the size of the tyres, and the time of exposure of the tyre to the liquid (Edil T.B., 2007).

It has been demonstrate that factors such as pH, size and particles aggregation deeply influence the elution process of substances from tyre. Also the amount of Zn leached from particles is related to their aggregation rather than their quantity (Gualtieri, M.et al., 2005).

Twin City Testing Corporation used extraction liquids having pH of 3.5, 5.0, 7.0, and 8.0 (the aquatic environment is typically described by the pH of the extraction liquid). The study showed that higher metal concentrations were obtained in the leachate when the pH was 3.5 (low pH). Higher hydrocarbons concentration was observed when the pH was 8.0 (high pH) (TCTC, 1990).

It has been reported that both new and old tyre chips leached organic and inorganic compounds, but at concentrations lower than the Toxicity Characteristic Leaching Procedure (TCLP) limits to be classify as hazardous material (TCTC, 1990) and (RMA, 1990). Newer tyre chips leached slightly higher concentrations of polycyclic aromatic hydrocarbons (PAHs) (TCTC, 1990).

It is important to note that in many studies the extraction liquid or test setup was designed *for worst case conditions that do not necessarily exist in the environment that tyre chips/granulate are used*. For example, laboratory tests performed with fixed volume of liquid or tyre chips/granulate exposed to aggressive extractions do not simulate conditions likely to exist in most tyre chips/ granulate applications. Thus, in the field studies, lower concentrations are likely to exist (Edil T.B., 2007).

Materials that can leach from tyre granulate can be broadly classified into two categories; organic compounds and metals. The rest of this section discusses the properties of granulate with respect to these categories.

Leaching of Organic Compounds

In a study aimed at checking the leaching of substances from drainage water and its environmental effect. The leaching of anti-oxidizing compounds from tyre shreds (5-30cm) used in the construction of a large light fill noise barrier on the highway in Norway was carried out. Three year leaching test report concludes that the leaching of Bisphenol-A, Nonylphenol or Octylphenol from tyre shreds induces no environmental risk if applied under given design condition (Edeskär, T., 2004).

Analysis of total organic compounds composition of tyre rubber granulate by Norwegian Building Research Institute (NBI); showed that PAHs, Phenols and Phthalates, were demonstrated in all the rubber granulate from tyre (samples 1, 2 and 5) (NBI, 2004). Thus attention should be paid to such compounds in considering the use of tyre granulate for product manufacture. This is necessary considering Swedish environmental objective of *A Non-Toxic Environment* that substances which are persistent, bioaccumulative and carcinogenic must be phased out. PAHs, Phenols and Phthalates exhibit some of these properties (KemI, 2006).

PAHs

Polycyclic aromatic hydrocarbons PAHs are present in high aromatic (HA) oils. Aromatic oils are used as plasticizers during tyre manufacture. Most of the PAHs in the oil are persistent, bioaccumulative and carcinogenic.

Phenols

Alkyl phenols are used as antioxidants in tyre. They are not chemically bound to rubber polymers thus can leach from the material. They are persistent and bioaccumulative and they give long term effect on the environment.

The presence of 4-t-octylphenol and iso-nonylphenol was demonstrated in both rubber granulates. Nonylphenol and octylphenol were found in the leachate.

Phthalates

These are used as solvents and plasticizers in plastics. They are not chemically bound to rubber polymers thus can leach from the material. Certain phthalates are reprotoxic (suspected to affect human reproductive health).

Dibutylphthalates (DBP), Benzylbutylphthalate (BBP) and Diethylhexylphthalate (DEHP) were demonstrated in all recycled rubber granulates. Phthalates were also detected in the leachate.

Leaching of Metals

The total metal composition of tyre granules was analyzed by NBI, 2004. The report indicates that lead, cadmium, copper and zinc were demonstrated in all tyre granulates. The recycled rubber granulate types values for lead, cadmium, copper, chromium, mercury and nickel are below the Norwegian Pollution Control Authority's normative values for most sensitive land use. However, the total concentration of zinc exceeds the Norwegian Pollution Control Authority's normative value for recycled rubber granulates.

The leaching test showed that zinc was transferred from granules to water. The zinc values are above the Norwegian Pollution Control Authority's limit for zinc in water in Environmental Quality Class V (very strongly polluted), but lower than the zinc concentration permitted in Canadian drinking water (5 mg/l).

The overall conclusion of these studies is that tyre shreds may increase levels of certain metals (e.g., iron and manganese) and some organic compounds; however, as concluded by Humphrey and Swett, 2006 in a detailed literature review report, there appears to be limited effect on drinking water quality of groundwater from leachate derived from tyres for a range of applications involving tyres or tyre shreds, *so human health concerns are minimal* (Edil, T.B., 2007).

3.2.2 Emission Properties

Emission is the giving off of gases from processes. Within the context of this review, emission implies the giving off of substances either in gaseous or in particulate form from tyre granules.

Swedish Guideline and Limiting values:

Swedish legislation governing the workplace environment, ‘Occupational Exposure Limit Values and Measures against Air Contaminants’ states that the air pollutant occupational exposure limits valid for adults for one working day has the hygienic limit value for PAHs (measured as benzo(a)pyrene) set as 0.002 mg/m³ (KemI, 2006). For outdoor air, the limiting value set for PAHs (measured as benzo(a)pyrene) is 0.1ng/m³, this is to be achieved by the year 2020 (KemI, 2006).

At the same time, the air pollutant occupational exposure hygienic limiting value for lead is 0.1 mg/m³ (total dusts); according to Swedish workplace environment legislation. For pollutants in out door air the limiting value (measured as annual mean exposure) for heavy metals (measured as lead) is 0.5 µg/m³.

Tables 3.2 and 3.3 show results from Swedish measurements in halls with synthetic turf made from tyre granulate.

Table 3.2: Measurement of Air in Swedish Halls Using Synthetic Turf, Relative to Limiting Values for Occupational Exposure. Source: KemI, 2006.

	Spånga [*]	Södertälje ^{**}	Limiting Value for workplace environment
PAH⁺ (ng/m³)	0.2	0.6	2,000
Lead (ng/m³)	0.1	<1	100,000

* Values from ‘Air-Borne Pollution in Football Hall with Synthetic Turf’, Stockholm Municipality, 2004.

** Values from ‘Air-Borne Pollution in Football Hall with Synthetic Turf’, IVL, 2004.

⁺ Measured as benzoapyrene.

The report on Air-Borne Pollution in a Football Hall with Synthetic Turf (IVL and Södertälje Municipality, 2004) states that the calculated level of benzoapyrene (0.075ng/m³) measured during activity in the hall was under the target value for the year 2020 for outdoor air (0.1ng/m³). Also the value for lead was significantly below the set limit.

Table 3.3: Measurement of Air in Swedish Halls Using Synthetic Turf, Relative to Limiting Values for Indoor Air. Source: KemI, 2006.

	Spånga [*]	Södertälje ^{**}	Limiting Value for outdoor environment
PAH⁺ (ng/m³)			0.1 ⁺⁺
PM_{2.5}	0.008	0.075	
PM₁₀	0.03	-	
Lead (ng/m³)			5,000
Total	-	<1	
PM_{2.5}	0.000007	-	
PM₁₀	0.00003	-	

*Values from 'Air-Borne Pollution in Football Hall with Synthetic Turf', Stockholm Municipality, 2004.

**Values from 'Air-Borne Pollution in Football Hall with Synthetic Turf', IVL, 2004.

+Measured as benzoapyrene.

++Target Value to be achieved by the year 2020.

The Norwegian Institute for Air research (NILU), in its assessment of three halls made with synthetic turf noted that, the air-borne dust in Halls 1 (Manglerudhallen) and Hall 2 (Valhalla) contained significant amounts of rubber from granulate, 50% in Hall 1 and 35% in Hall 2. The air-borne dust in all three halls contained PAHs and phthalates Table 3.4 shows the measured PAHs and Phthalates in the Halls (NILU, 2005),.

Table 3.4: Air Measurements in Norway Synthetic Turf Halls. Source: NILU, 2005.

	Manglerudhallen	Valhalla	Östfoldhallen
PAH*(ng/m³)			
PM₁₀	1.15	0.56	0.38
Gas phase	0.02	<0.01	0.01
Phthalates** (ng/m³)			
PM_{2.5}	37.3	81.2	84.9
PM₁₀	131.4	134.4	117.1

*Measured as benzoapyrene.

** Total phthalates.

The concentration of volatile organic compounds (VOCs) was higher in the two halls (Hall 1 and Hall 2) that contain granulate from recycled rubber than it was in the hall with granulate of thermoplastic.

3.2.3 Migration Analysis

Nilsson, N. H. et al., 2005 analyzed PAHs and aromatic amines content in tyres; it also carried out screening and quantitative analysis as well as migration tests. Result from the investigations shows that

- Tyres contain PAHs and benzo(a)pyrene can be used as a PAH-indicator. Migration test shows that only the most water soluble PAHs and aromatic amines migrate from the tyre rubber to the sweat.
- It was preliminarily concluded that migration from the tyre is not a significant source for the PAHs contamination of the sand. The results indicate that the PAHs content in the sand originates from atmospheric deposition.

- Health Assessment:

The potential migration of PAHs and aromatic amines, to child skin playing with tyres was investigated. In the worst case it was assumed that a skin area of 200 cm² on the thighs of a child is exposed for an hour five times a week during one year.

From the results it was concluded that the potential health risk related to the use of discarded tyres on playgrounds is insignificant. The marginal of safety (MOS) is high for all the identified components. Thus does not pose health risk.

3.2.4 Ecotoxicology

Ecotoxicology is the study of the harmful effects of chemical compounds on species, population and the natural environment.

Eco-toxicity study is necessary when considering the use of tyre granulates for product development since studies have shown that certain substances can leach from tyre granulate, thus this study is to ascertain the potential harm such leachates could cause in the ecosystem during use. Table 3.5 shows the result of ecotoxicological study on tyre rubber granulate as reported by Basel Convention, 1999.

Table 3.5: Ecotoxicological test results expressed as averages. Source: Basel Convention, 1999.

Test feature	Specie	Organism	EC50 (exposure time)	LC50 (exposure time)	Test method
Growth	Algae	S.Capricornutum	> 13 000 mg/l (72h)		NF EN 28692/ ISO 8692
Mobility	Small shellfish	Daphnia magna	> 69 000 mg/l (24h)		NF T 90 301/ ISO 6341
Mortality	Fish	Brachydano Rerio		> 58 000 mg/l (24h)	NF T 90 303/ ISO 7346-1

EC50 is the corresponding raw material concentration in water at which the growth (algae) or the mobility (small shellfish) is reduced by 50% after exposure time. LC50 is the corresponding raw material concentration in water at which 50% of the population die after exposure time.

Comparing with the ecotoxicological scale used in the European Union for the labelling of new chemical substances through the effects on aquatic organisms e.g.:

Very toxic to aquatic organisms if EC50 or LC50 <1mg/l

Toxic to aquatic organisms: 1mg/l <EC50 or LC50 <10 mg/l

Harmful to aquatic organisms: 10 mg/l <EC50 or LC50 < 100 mg/l

It was concluded from the results that the first ecotoxicological response (on algae) shows an order of magnitude of 130 times greater than the maximum concentrations at which it is acknowledged that a substance is harmful to aquatic organisms. Considering the exposure time for these studies (72h and 24h), it would not be possible to obtain this level of concentrations for the application of tyre granulate for oil decontamination since it is believed that the exposure time in this case will be for few minutes on the contaminated site.

3.2.5 Regulations on Tyre Composition

The environmental objectives set down by the Swedish parliament state that substances of very high concern should be phased out from newly produced articles (KemI, 2006).

Tyres contain several substances that are substances of concern. These substances may persist in the environment, they may be bioaccumulative, carcinogenic, reprotoxic, or mutagenic. This is true for polycyclic aromatic hydrocarbons (PAHs), phthalates and certain metals (KemI, 2006).

Sweden has been working actively within the EU to prohibit high aromatic oils in tyres. The EU decided in the summer of 2005 to introduce limits for the concentrations of PAHs in newly manufactured tyres. The new regulations will come into force in 1st January, 2010 (EU Directive on PAHs, 2005). This will in the long term lead to lower levels of PAHs in the rubber from recycled tyres. Thus will make recycled tyres more environmental friendly for products development.

The Swedish National Chemicals Inspectorate proposed in Ordinance on the Prohibition of Highly aromatic Oils in Certain Tyres (KemI, 2003):

- All oils must not be used in the manufacture of tyres if it fulfils the criteria of carcinogenicity, and contains more than 10 ppm in total of the twelve designated PAHs or more than 1 ppm of benzo(a)pyrene.
- Tyres will not be regarded as containing PAH oil if the concentration of PCA (PAH + aromatics substituted with nitrogen, sulphur or oxygen compounds) is less than 10% in measurement according to the following methods:
 - ✓ SS 155116 Petroleumprodukter
 - ✓ SS-ISO 1407 Edition 1. Gummi
 - ✓ SS-ISO 4645 Edition 1. Gummi och gummiprodukter

Tyres contain about 1.5% by weight of hazardous elements or compounds listed in Annex 1 of the Basel Convention. These are encased in the rubber compound or present as an alloying element. Tyre composition of these substances is shown in Table 3.6, thus in the use of tyre granulate in product manufacture consideration should be given to the fact that such substances must not be emitted or leached into the environment above the designated limits.

Table 3.6 : Basel Convention hazardous waste constituents of Tyres

Source: Basel Convention, 1999.

Constituent	Chemical Name	Remarks	Content (% weight)
Y22	Copper Compounds	Alloying constituent of the metallic reinforcing material (Steelcord)	Approx. 0.02 %
Y23	Zinc Compounds	Zinc Oxide, retained in the rubber matrix	Approx. 1 %
Y26	Cadmium	On trace levels, as Cadmium compounds attendant substance of the Zinc Oxide	Max. 0.001 %
Y31	Lead Lead Compounds	On trace levels, as attendant substance of the Zinc Oxide	Max. 0.005 %
Y34	Acidic solutions or acids in solid form	Stearic acid, in solid form	Approx. 0.3 %
Y45	Organohalogen compounds other than substances in Annex	Halogen butyl rubber (tendency: decreasing)	Content of halogens max. 0.10 %

3.3 Absorption and Environmental Properties Discussion

The material composition of tyre has made it possible for tyre granulates to have an intrinsic tendency to absorb certain substances. Several research results highlighted pointed consistently to the absorption abilities of tyre granulates and tyre chips.

Result from Aisien, F. A. et al. (2002), demonstrated clearly that tyre granulate have potential to be used in oil spill clean up, because of its intrinsic ability to absorb oil. It equally demonstrated that granulate particles size and temperature has significant effect on the absorption rate of tyre granulate. Absorption rate increases with decrease in both particles size and temperature. It was further stated that presence of water does not have a significant influence on the absorption capacity of granulate thus can be used in oil combating in open sea, rivers and creeks. It was equally noted that regenerated rubber granulate is less efficient than fresh rubber in oil clean up.

Other researches equally showed the potentials of tyre granulate to absorb petroleum hydrocarbons which include gasoline, oil, grease and VOCs such as benzene, toluene,

xylene etc. They also highlighted the ability of tyre granulate to absorb certain metals such as arsenic, cobalt, lead, nickel, selenium, mercury and barium. Tyre granulate ability has equally been demonstrated in removal of anionic surfactants (sodium dodecyl sulfate) in aquatic environment in which 90.97% removal was achieved.

It has also been found that organic compounds are sorbed *primarily* onto tyre rubber polymeric materials styrene butadiene rubber (SBR) and partially onto other materials present in tyre granulate such as carbon black, (Kim et al, 1997). SBR is one of the major components of tyres and is non polar. Thus non polar organic compounds such as benzene, toluene, trichloroethylene, and tetrachloroethylene and others are attracted to it.

Tyre chips/granulate have demonstrated better absorption capacity (1.4 to 5.6%) when compared to activated carbon, Park et al. (1996). It was also found that of the organic compounds sorbed in tyre chips, only 3.5 to 7.9% were desorbed. Thus it has good sorbate retention ability.

The review of absorption properties of tyre granulate has shown that it could be a good sorption material for hydrocarbon based materials and some metals especially in areas of high contamination; this could be explored for environmental benefits both as a way of finding sustainable use of end-of-life tyres as well as keeping our environment clean.

It will be a step in the right direction to conduct research with direct focus on investigating tyre granulate ability in oil decontamination on different types of oil that may be encountered in an oil decontamination situation here in Sweden.

Substances that leach from tyre granulate could be of organic or inorganic origins. Edil, T.B. (2007) noted that in many studies, the test setups were designed *for worst case conditions* that do not necessarily exist in the environment that tyre chips/granulate are to be used in.

Factors that have been identified to affect the leaching of compounds from tyre granulate include: the pH, size and particle aggregation, age of tyre, time of exposure of tyre to liquid, aquatic environment and test conditions. New tyres were found to leach more PAHs than older tyres, this is due to the wearing away of tyre tread with time during its use in automobile vehicles.

It is a fact that tyre granulate contain some substances classified as hazardous according to Basel Convention, 1999. Analysis of three different samples of tyre granulate has shown that the material contains organic compounds of attention such as PAHs, Phenols and Phthalates. The point is to what extent do they contain and at what quantities can these substances leach or be emitted to the environment under normal conditions? Do these values exceed the limit values?

NBI reports that total concentration of PAHs in tyre rubber granulate exceeds the Norwegian Pollution Control Authority's normative value for all the three tyre granulates but PAHs leachate complies with the requirements in the Drinking Water Regulation.

4-t-octylphenol and iso-nonylphenol were present in tyre rubber granulates. The concentrations of nonylphenols in granulate and leachate exceeded the limit for Canadian Environmental Quality Guidelines and the predicted no effect concentration (PNEC) value for water respectively.

DBP, BBP and DEHP were present in all the recycled rubber granules. Phthalates were equally present in the leachate (NBI, 2004).

Lead, cadmium, copper and zinc were present in all tyre granulates but the values for lead, cadmium, copper, chromium, mercury and nickel are below the Norwegian Pollution Control Authority's normative values for most sensitive land use but is exceeded by zinc. Leaching test shows that zinc is transferred from granulate to water and zinc values in the leachate exceeded the limit Norwegian Pollution Control Authority's but is lower than the zinc concentration permitted in Canadian drinking water (5 mg/l) (NBI, 2004).

Regarding to the emission properties of granulates; the calculated values of PAHs (measured as benzo(a)pyrene) and heavy metals (measured as lead) were below the values set for Swedish out door air and work place environment in halls made with synthetic turf from tyre granulate. However NILU, 2005 noted that the concentration of VOCs was higher in the hall that contain granulate from recycled rubber.

Migration tests show that tyres are not significant source for PAHs contamination of sand. Also, the marginal of safety is high for all identified components in migration analysis for tyres in children play ground, thus discarded tyres does not pose significant health risk.

3.4 Absorption Mat Prototype Development

For the development of absorption mat, consultations were held with experts in the industry in the area of rubber processing regarding possible methods of producing such product; absorption mat based on recycled tyre rubber..

From the reviews conducted so far, it has been demonstrated that tyre rubber granulate has the ability to absorb oil and other organic compounds. The task in developing the product may be divided into:

- Manufacturing Process
- Suitable Shape

3.4.1 Manufacturing Process

Tyre rubber granulate are loose particles. Binding is a way of putting the tyre granulates together into different forms of absorbent so that it could be easily handled during decontamination operation. For the manufacture of absorption mats, at least three different types of binders could be used which determines the manufacturing method to use (Levin, N. 2007):

Using Polyurethane Binder: The manufacturing process should be the simplest with polyurethane. The only disadvantage of polyurethane may be that it has a good oil resistance and will therefore probably decrease the oil absorption.

Using Rubber Latex: This could be a simple method; it can be done by mixing with granulate in an open mixer, dry and cure the mats in some type of press.

Using Rubber Reclaim: A rubber reclaim is partly devulcanized rubber from tyre treads. This method will require a rubber mixer for blending granulate and reclaim, and has to be cured at a high temperature. From the cost aspect this can be the cheapest due to the reasonable cost of reclaim. And as an extra bonus the mat will be all recycled material beside some percentage of curing agents.

3.4.2 Suitable Shape

Efficiency of the absorption mat will also depend on the shape of the product in which they are made of. Since the shape of the mat will determine the amount of area exposed for absorption of oil at a time which in turn affect the absorption rate of the mat. This factor however has to be combined with ease of manufacturing process.

The following shapes are being considered:

- Pads / Mats: They will be continuous absorbents which will be shaped such that their length and width will be much greater than their thickness. They could be rectangular or square shaped.
- Rolls: These will also be continuous absorbents (pads / mats) which have been rolled to form cylindrical shape.
- Enclosed shape (e.g. booms, pillows): In this case tyre rubber granules will be enclosed with either fabric, mesh or netting in order to enhance their ease of use for oil decontamination.

3.4.3 Disposal Method

The disposal method for used absorption mat is another important factor to consider in the development process of the absorption mat. This is because used absorbents themselves could constitute environmental problems (EPA, 2006). Equally, the disposal should be carried out in accordance with local, state and national legislation.

The following methods are being considered for the used absorption mat disposal:

Reuse

Reuse of this material for oil decontamination implies finding an efficient method for removal of the absorbed oil (oil recovery) from the rubber matrix so that it can be clean and used again. But, considering the fact that tyre rubber granulate are polymeric material, this method might not be cost effective.

The following methods may be used in extracting the oil from used granulates:

- **Compression:** The release of oil from absorbent polymeric materials is not possible by squeezing (ITOPF, 2006)
- **Regeneration:** Regeneration could be thermal (using water vapor, hot air or vacuum vapor) or solvent extraction (using certain chemicals) or combination of both.

Regenerated rubber tyre granulate loses up to 46% of its absorption capacity when compared with fresh rubber granulate (Aisien, F. A. 2002). It was noted that that the swell of the mats will be very high when used, thus it will be more or less impossible to reuse them and difficult to handle for a thermal regeneration (Levin, N., 2007). It indicated that by swelling the tensile strength of the mat will decrease rapidly.

Apart from these deficiencies, regeneration will also involve the use of energy and possibly chemicals. These will added to the overall cost of the regenerated product.

Recycling

Rubber granulate is a polymeric material, thus could be depolymerized at elevated temperatures to release the oil while recovering the materials in different form (ITOPF, 2006). The recovered material could be useful in other application. This method however implies the use of high temperatures thus energy cost is a strong factor to consider.

Incineration

The largest fraction of end-of-life tyres today are used as Tyre Derived Fuels (TDF) in industries e.g. in cement kilns. This is due to high calorific value (15,500 BTU/lb) of TDF. Its calorific value is higher than that of coal and next to natural gas. This high calorific value will even be increased further when granulate is used to absorb oil.

Used mat will have about 30-50% oil! This will be an excellent energy source. Cement kilns and many incineration stations producing hot water and electricity prefer to use some tyres as fuel together with other scrap due to the high energy content. Incineration disposal option was favoured (Levin, N., 2007).

Incineration may be a suitable disposal option due to the fact that absorption mat is not only disposed but energy is also produced (rather than consumed) in the process. Consideration should however be taken on the possible emissions associated with incineration.

3.4.4 Market Potentials

Absorbents have very good market potentials with respect to oil decontamination. ITOPF reports that of about 10,000 oils spill incidents on record; 84% are small spills and

absorbents have been found to be the most suitable method for decontamination of small spills (ITOPF, 2006). The use of absorbent materials, provided it is environmentally friendly, easily recoverable, of low cost and effective absorbent has proved to be the fastest way of combating oil spillage (Labelle et al., 1994).

Records from Swedish Rescue Service Agency (SRSA) shows that about 2200 hazardous chemical spills are recorded each year; more than half of these spills are small spills which are decontaminated using absorbents (McIntyre, C., 2007). In 2006 alone, a total of 1708 chemical spill decontamination operations were carried out by SRSA, of these decontamination operations absorption method was used in 1294 cases representing 76% of the method used in spill decontamination operations. Thus of all spill decontamination methods, absorbents is the most commonly used, therefore it has the highest market.

Presently, in Sweden the common absorbents used in oil decontamination are Absol (calcium, clay material); Zugol and Ecobark (wood derived materials). Absol being clay material is not suitable for oil decontamination in water (EPA, 2006), due to its density while Zugol and Ecobark are wood derived products thus absorb only about its own weight in oil. Large quantity of these material will therefore be required for effective decontamination, this creates both cost and storage problems.

Tyre rubber has been reported to absorb four to five times its weight of oil (Prudnikov and Smtanjuk, 1994; Perry and Chillton, 1983). Absorbents from tyre rubber granulate will find application in indoor, outdoor as well as land and water decontamination operations. Thus this has better absorption capacity and will find application in any location of spill. This material is a waste material therefore apart from making it a unique approach for management of end-of-life tyres; it will also make the absorption mats cheaper than its counterparts in the market. Not only that, uptake of oil by tyre rubber granulate will enhance its calorific value making it an excellent fuel for cement kiln and energy industries. These potentials cannot be found in current absorbents in the market.

Granulate works best with low viscous oils (100 -200 centistokes); this includes light products: e.g. diesel, fuel oil 1, kerosene, aviation fuel, hydraulic oils, lubricants, light crude oil. Absorption mats will be suitable for indoor oil decontamination application e.g. car workshop, factory, machinery operation, garage, boat etc. (also in harbors where small spills are common). These are the potential buyers of this product; however, the market is not so big in Sweden (Fejes, J., 2007).

The information so far gathered from review of literatures, consultations with agencies and experts in oil decontamination operations and the current market situation has shown that absorbents in particular absorption mats from tyre rubber granulate has good market as far as oil decontamination is concerned.

4. EXPERIMENTS ON TYRE GRANULATE

For the use of tyre rubber granulate for the development of absorption mats for oil decontamination it is necessary that the granulate material have good absorption properties at the same time be environmentally friendly during its application for this for this purpose. It therefore becomes necessary to conduct tests on the tyre rubber granulates to ascertain its properties in with respect to these properties. Two types of tests were carried out on the tyre rubber granulate.

- Absorption Properties Tests
- Environmental Properties Tests

4.1 Absorption Properties Tests

4.1.1 Materials

The following facilities were used for the experiment on absorption properties of tyre rubber granulate:

- Mechanical shaker with sieve sizes; 0.5 mm, 1.00 mm and 2.00 mm
- Weighing balance
- Beakers (1 litre), 5 pieces
- Water Bath
- Ice
- Stop watch
- Granulate samples: The following granulate samples were supplied by the tyre granulate company IMDEX AS, Denmark.
 - ✓ 0.0-1.4 mm
 - ✓ 0.0-2.0 mm
 - ✓ 0.8-2.0 mm
 - ✓ 1.4-2.5 mm
- Oils:
 - ✓ Oil A = 15W- 40: Super Gold
 - ✓ Oil C = 15W- 40: Inboard (Shell Nautilus)
 - ✓ Oil D = 10W- 40: Shell Helix Plus Diesel (Engine Clean Up)
 - ✓ Oil E = 5W- 40: Shell Helix Ultra (Fully Synthetic Motor Oil)
 - ✓ Oil F = Gasoline (E95)
 - ✓ Oil G = Diesel

These oils were selected for this test based on consultations with experts on oils that could be encountered for the intended applications of the absorption mat for indoor and outdoor oil decontamination including motor boats. Consideration was also given on viscosity of the selected oils which was suggested to be low viscose oil about, 100 centistokes (Fejes, J., 2007).

4.1.2 Sample Preparation

Mechanical shaker (Octagon 200, Test Sieve Shaker) was used for separation of the tyre rubber granulate into the desired fractions using the sieve sizes 0.5 mm, 1.00 mm and 2.00 mm. The separation was carried out at an amplitude setting of 8 while the shaking lasted for 20 minutes in each case. Figure A1 in the Appendix presents the mechanical shaker used for the separation procedures.

The shaker separated granulates into 0.5-0.9 mm, 1.00-1.99 mm and 2.00-3.99 mm fractions. But for easy notation, these are represented as:

- 0.5-0.9 mm fraction = 0.5 mm
- 1.00-1.99 mm fraction = 1.00 mm
- 2.00-3.99 mm fraction = 2.00 mm

An illustration of the different fractions of the separated granulate fractions is shown in figure 4.1.

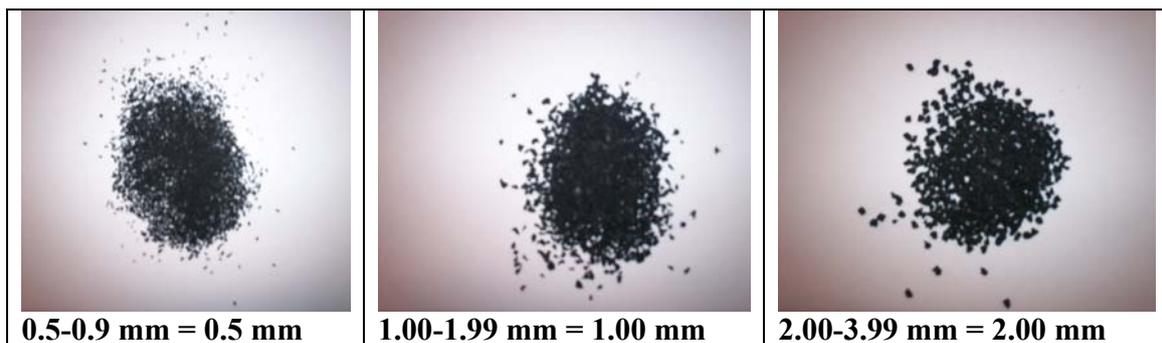


Figure 4.1: Different Fractions of Tested Granulate Samples.

4.1.3 Experimental Procedure

4.1.3.1 Oil Only Absorption Studies

A set of five samples, 10g each of tyre rubber granulate was weighed using the weighing balance KERN EW6200-2NM. The sieves from the mechanical shaker were weighed to obtain their initial mass. 100 ml of test oil was measured into each of the 5 beakers. Beakers with oil sample were placed firmly into the water bath with thermometer placed directly into one of the beakers to measure the exact temperature of the oil. The water bath was warmed by temperature adjustment or cooled with ice until the desired temperature is maintained in the thermometer. Granulate samples (10g) were then added into each of the beakers and the timer started. Beakers were removed separately and sieved after time intervals of 5min, 10min, 20min, 30min, and 40min. Granulate with the absorbed oil was weighed together with the sieve after the last drop of oil has been observed. Values were recorded.

This procedure was repeated for all oil samples tested and at temperatures 10°C, 20°C, 25°C and 30°C. Only Oil A was tested at 25°C. The oils were tested with granulate fractions 0.50, 1.00 and 2.00mm.

Table A1 in the appendix shows the order of the absorption test experiments conducted on the tyre rubber granulate.

4.1.3.2 Oil / Water Mixture Absorption Studies

The same procedure for oil only was followed but in this case rather than using 100ml of oil, oil and water was mixed in ratio 1:5 v/v i.e. 100ml of oil was mixed with 500ml water. Only diesel (Oil G) and water mixture were tested in this case.

4.1.3.3 Water Only Absorption Studies

Same procedure was followed for the studies.

Figures A2 and A3 in the Appendix are the illustrations of the oil/water mixture before absorption studies and experimental set-up during oil/water mixture absorption studies respectively.

4.1.3.4 Calculations of Oil Absorption

If; a = Initial Mass (g) of Sieve before adding of used granulate
 b = Final Mass (g) of Sieve after adding of used granulate
 c = Mass of granulate sample (10g)

Mass of Oil (g) Absorbed by Rubber Granulate = $b - (a + c)$

Oil Absorption [(g) oil/ (g) rubber granulate] =
$$\frac{\text{Mass of Oil Retained by Rubber Granulate}}{\text{Mass of Rubber Granulate}}$$

4.1.4 Results and Discussion

Figure 4.2 is an image of a single 2.00 mm granulate sample before absorption of diesel and after 30 minutes absorption period.

The areas covered by granulate before and after diesel absorption was measured with microscope (Nikon SMZ800). The result shows the area before absorption to be $\approx 5077215.86 \mu\text{m}^2$ (5.077 mm^2) while after absorption it was $\approx 7400308.50 \mu\text{m}^2$ (7.40 mm^2). This represents about 46% increase in area of granulate after absorption. This is because the diesel oil upon absorption into granulate causes the swell, thus resulting in increase in size of the particle; the oil has been retained in the tyre rubber granulate particle.

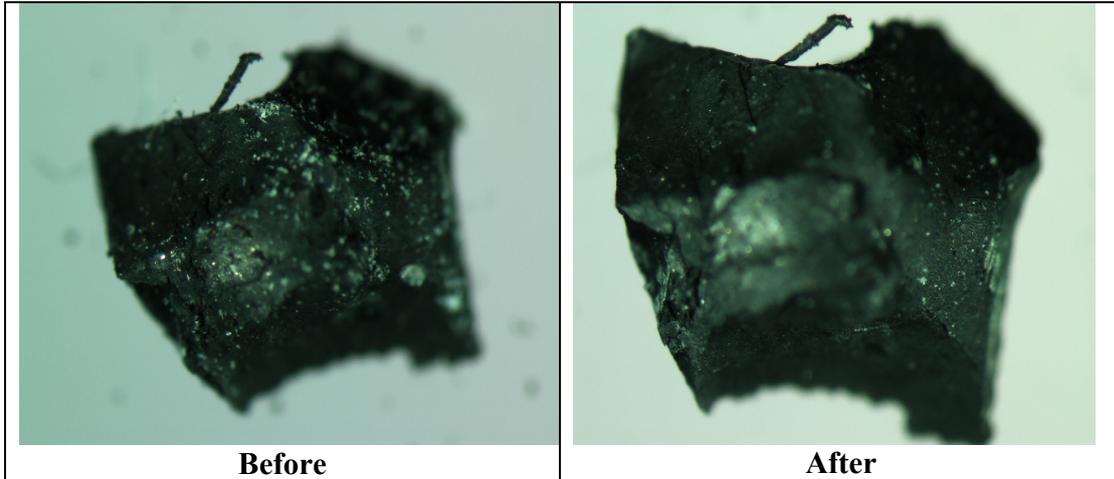


Figure 4.2: 2.00 mm Granulate Sample Before and After Absorption of Diesel (30 x magnification)

4.1.4.1 Granulate Size Effect on Absorption Capacity

Figures 4.3 and 4.4 are the plots illustrating the effect of particle size of rubber tyre granulate on oil absorption capacity. Figure 4.3 shows granulate size effect on the absorption of Oil A at 30°C while figure 4.4 is granulate size effect on absorption of oil C, D and E after 40 minutes.

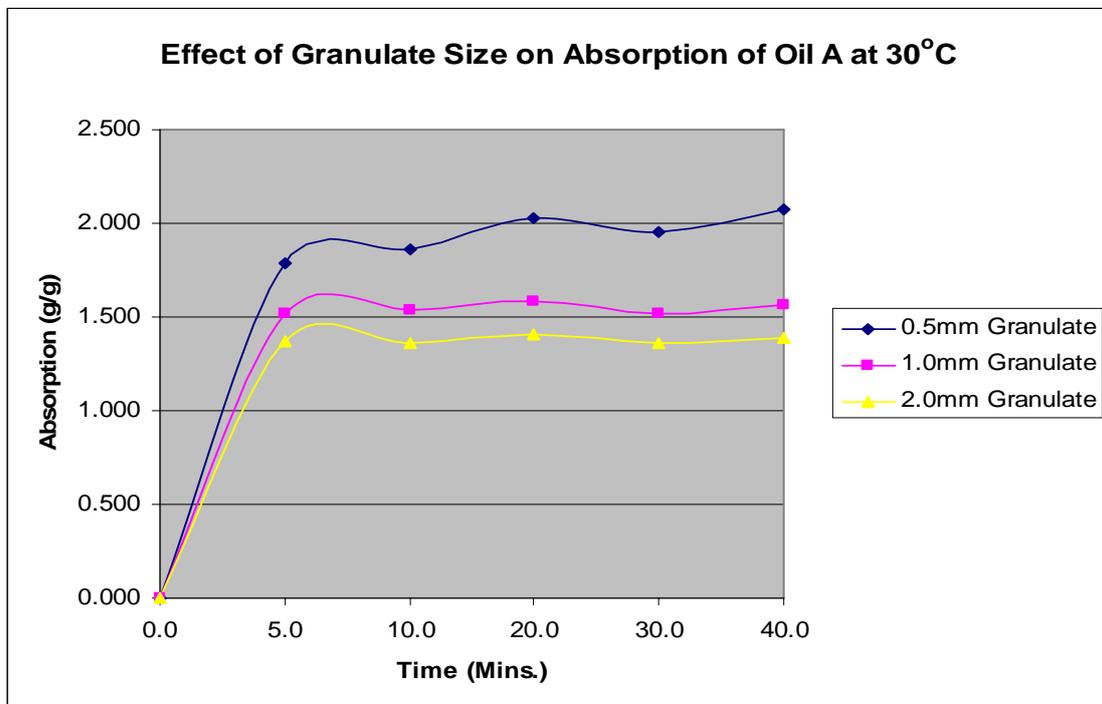


Figure 4.3: Granulate Size Effect on Oil A Absorption

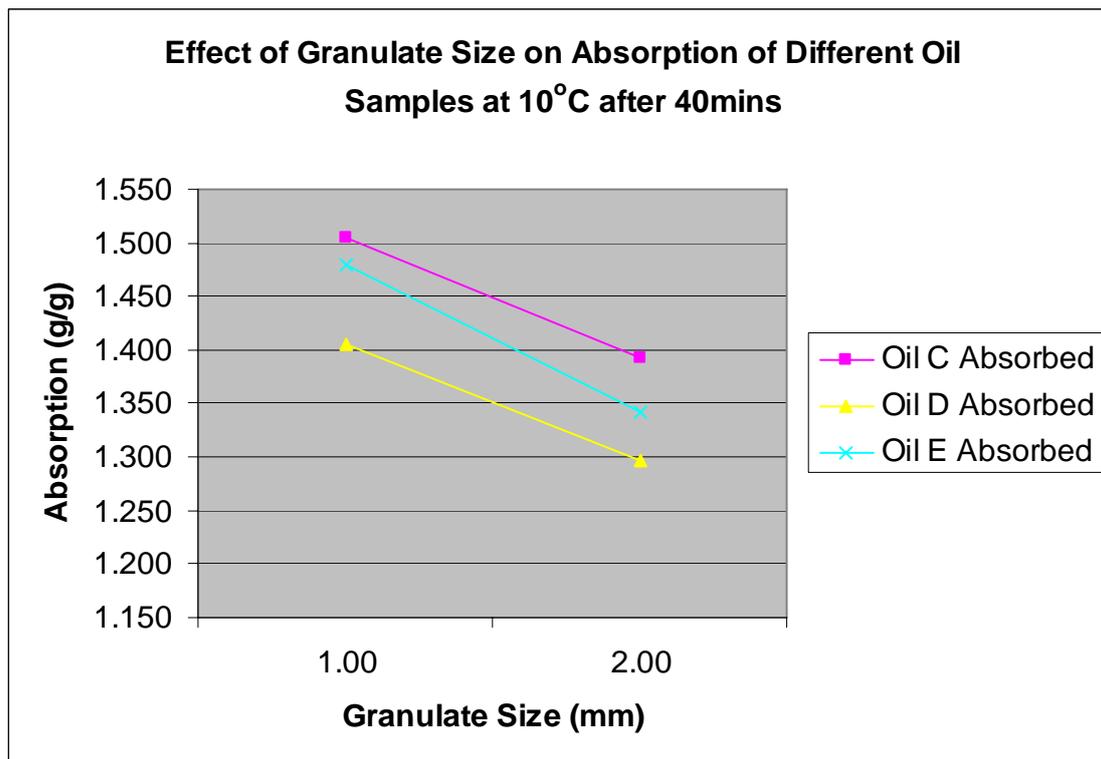


Figure 4.4: Granulate Size Effect on Absorption of Different Oil Samples

These plots show that at smaller rubber granulate particles sizes of rubber granulate, more oil absorption is recorded. For example in figure 4.3, highest absorption of Oil A was observed when the smallest granulate particle size (0.5 mm) was used. Likewise in figure 4.4 for all the different oil tested, absorption was higher with smaller granulate size (1.00 mm) than with bigger granulate size (2.00 mm).

This observation corresponds to the fact that decrease in particle size will result to an increase in the absorption due to increased surface area of the rubber tyre granulate.

Figures A4 - A6 in the appendix also show similar trend of the granulate size effect on absorption at 20°C, 25°C and 30°C.

4.1.4.2 Temperature Effect on Absorption Capacity

Effect of temperature on absorption capacity was demonstrated in figures 4.5 - 4.7. Figures 4.5 and 4.6 are the plots of temperature effect on absorption of diesel (Oil G) and gasoline E95 (Oil F) respectively while figure 4.7 is temperature effect on oils C, D, E, F and G tested with 1.00 mm granulate.

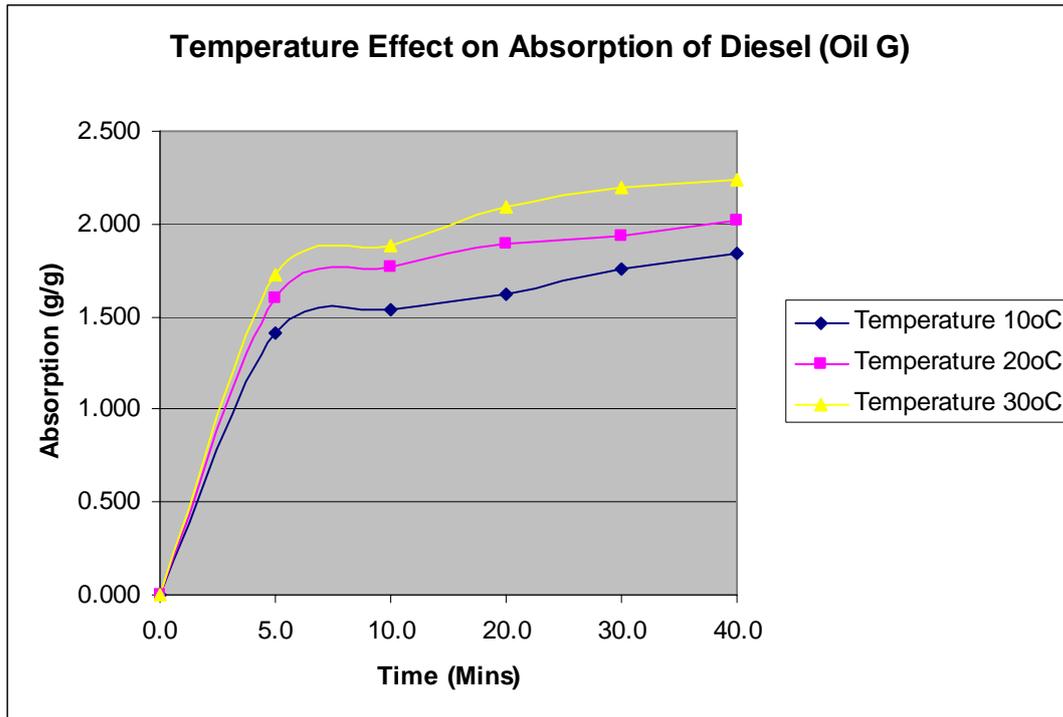


Figure 4.5: Temperature Effect on Absorption of Diesel (Oil G) in 1.00 mm Granulate

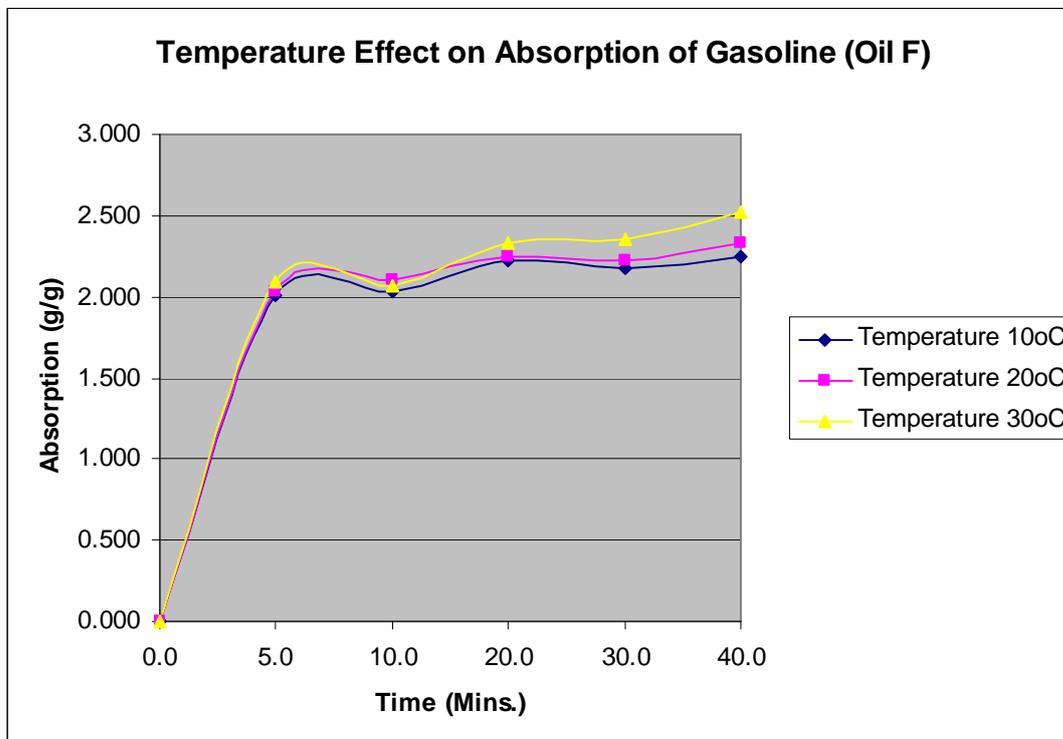


Figure 4.6: Temperature Effect on Absorption of Gasoline (Oil F) 1.00 mm Granulate

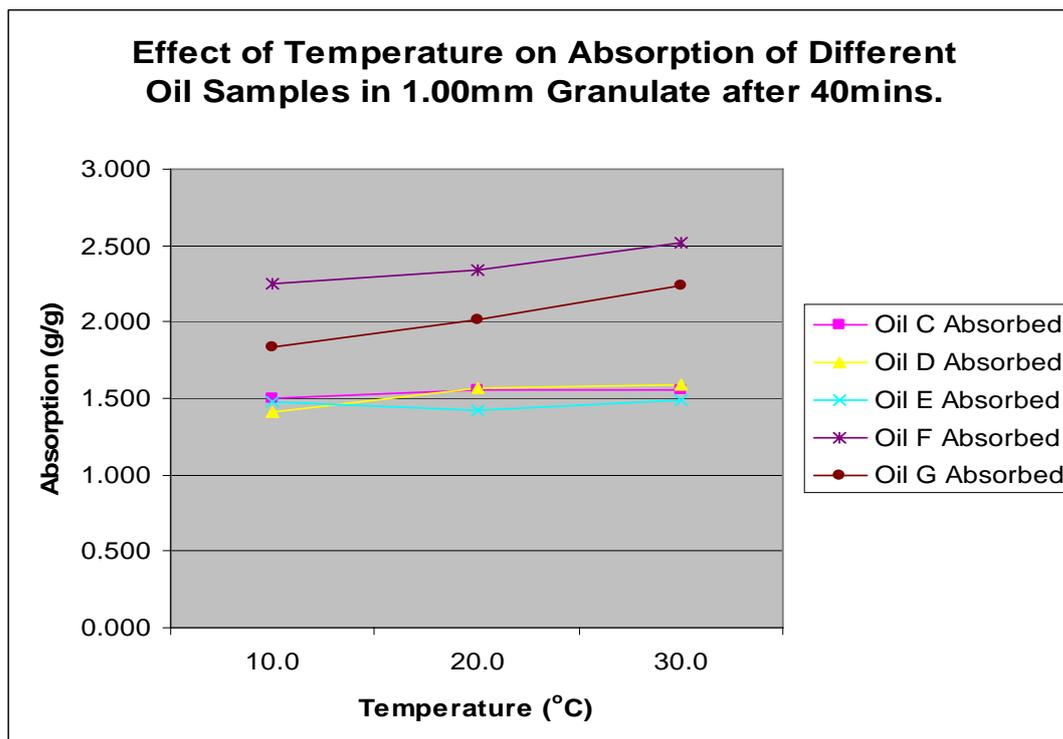


Figure 4.7: Temperature Effect on Absorption of Different Oil Samples

From the plots it can be observed that an increase in temperature up to 30°C generally results to a gradual increase in oil absorption by the rubber granulate. Highest absorption was recorded at 30°C in all cases. For example for diesel (Oil G) at 10°C absorption was 1.841 g/g after 40minutes while at 30°C absorption was 2.236 g/g this represents a 21.5% increase in absorption at 30°C and highest percent increase recorded. The least increase was recorded with Oil E; 0.67%.

This could be explained by the fact that up take of oil by absorbents is usually via capillary action (Bertrand P.A., 1993); which work by drawing liquid into the molecular structure of the material (ITOPF, 2006).

At lower temperatures, the oil molecules have less kinetic energy thus will not be able to migrate faster and deeper into the rubber granulate body structure; thus much of the oil will be retained by adsorption on the surface and pores of the rubber granulate. However at higher temperature the molecules migrate faster into the pores and body structure of rubber granules. The rubber granulate is a polymeric material thus will retain the oil molecules that were able to penetrate into its body structure (EPA, 2006) and (ITOPF, 2006).

Therefore since more oil can migrate into the body structure of rubber granulate at higher temperature, more oil are retained (absorbed) at such temperatures, hence increase in temperature resulted in increased absorption.

Figure A7 in the appendix also illustrates the temperature effect on absorption of Oil C, D and E in 2.00 mm granulate sample.

4.1.4.3 Oil Type Effect on Absorption

Figure 4.8 shows the results on the effect of oil types on absorption capacity of the tyre rubber granulate at 20°C.

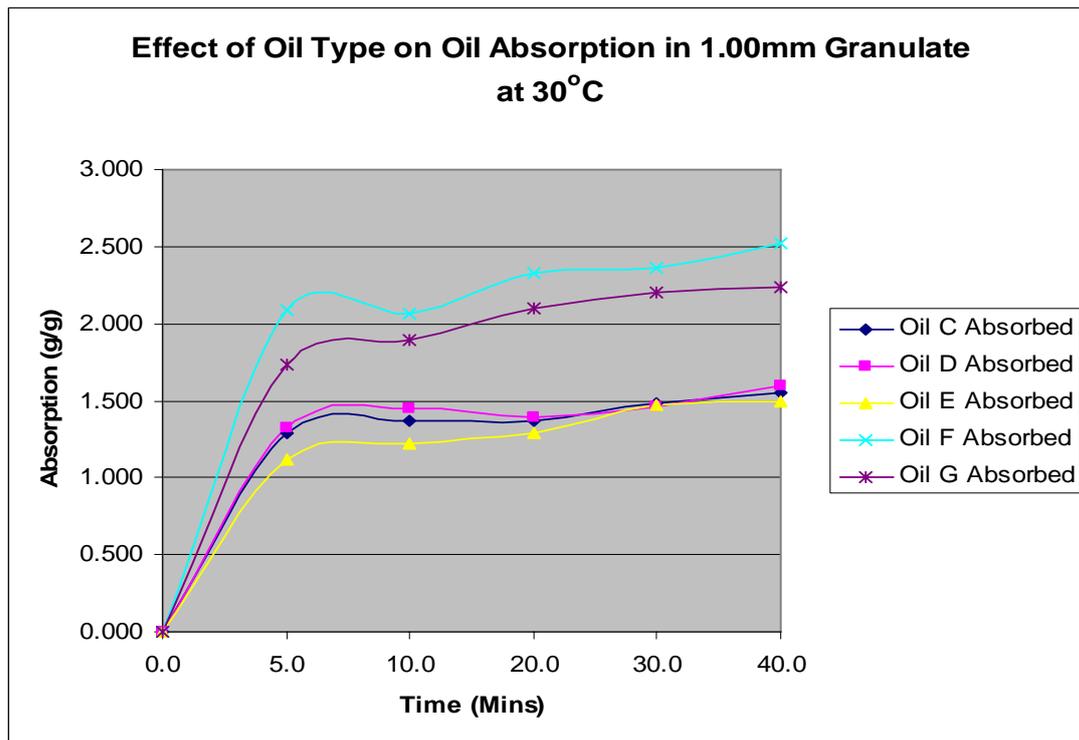


Figure 4.8: Effect of Oil Type on Absorption of Different Oil Samples

It can be observed from the figure that gasoline (Oil F) recorded the highest sorption (2.518 g/g) towards 1.00 mm granulate at 30°C after 40mins this is followed by diesel (Oil G). The lubricants; Oils C, D and E have the least sorption. Two factors could be responsible for this; the viscosity and the chemical composition of the oils.

Gasoline has very low kinematic viscosity; 0.40 mm²/sec at 40°C. Diesel has kinematic viscosities 2 to 6 mm²/sec at 40°C while the viscosity value for the oils C, D and E range between 70 to 100 mm²/sec at 40°C. These values thus show that oil absorption into granulate is related to their viscosity; it will be observed that the less viscous oils are absorbed higher than the more viscous oils i.e. absorption tends to decrease with increase in viscosity. This is also supported by the fact that more viscous oil will not be able to migrate deep into the body structure granulate while the less viscous oil will migrate faster and deeper.

Chemical composition of the lubricants (motor oils) could also be another factor that results in lower absorption observed with the lubricants. Safety Data Sheet, 2007; on oils

C, D and E show that lubricants contain additives such as detergents and dispersants (Zinc dialkyldithiophosphate (ZDDP) which also contain calcium). Encyclopedia reference on motor oil shows that part of the function of ZDDP and calcium additives in engine is to prevent the formation of sludge and varnish deposits, thus keeping the engine clean. Such additives will not allow oil to migrate and be retained inside the body structure of granulate. Dispersants have negative effect on the use of absorbents (ITOPF, 2006). Hence, tyre rubber granulate may not be a good absorbent for motor oils.

Crude oil absorption capacity was not studied here but available from Aisien, F.A., 2002. The study showed that crude oil absorption by tyre rubber granules resulted in higher absorption (up to 5g oil/g rubber granulate). This could be due to higher molecular weight fractions present in crude oil. Figure 3.1 shows variation of absorption at 30°C (303K) with rubber particle sizes (crude oil only).

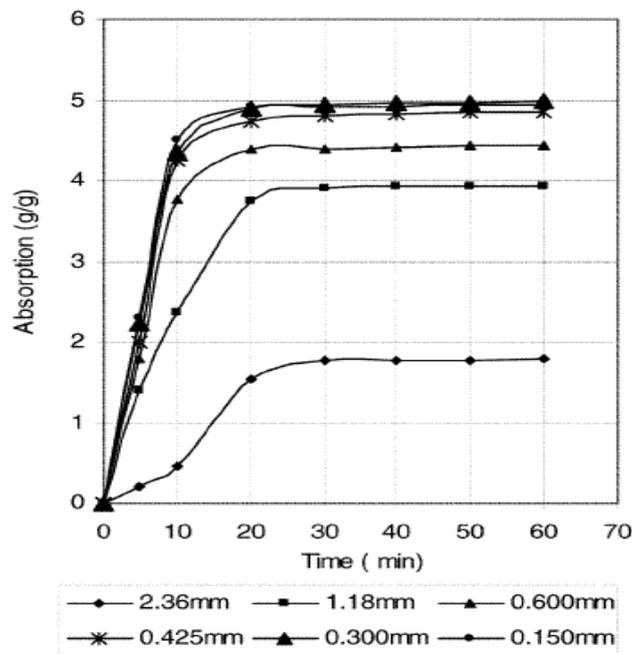


Figure 3.1: Variation of absorption at 30°C (303K) with rubber particle sizes (crude oil only). Source: Aisien, F. A. et al, 2002.

Figure A8 and A9 in the appendix show the effect of oil type on absorption of different oil samples at 10°C and 20°C respectively.

4.1.4.4 Oil/Water Mixture Effect on Absorption

Oil decontamination operations often occur in the presence of water for example in natural waters like lake, rivers etc. The experiments were conducted to ascertain if the presence of water has any effect on oil absorption by tyre rubber granulates. Figures 4.9 and 4.10 show the effect of oil/water mixture on absorption.

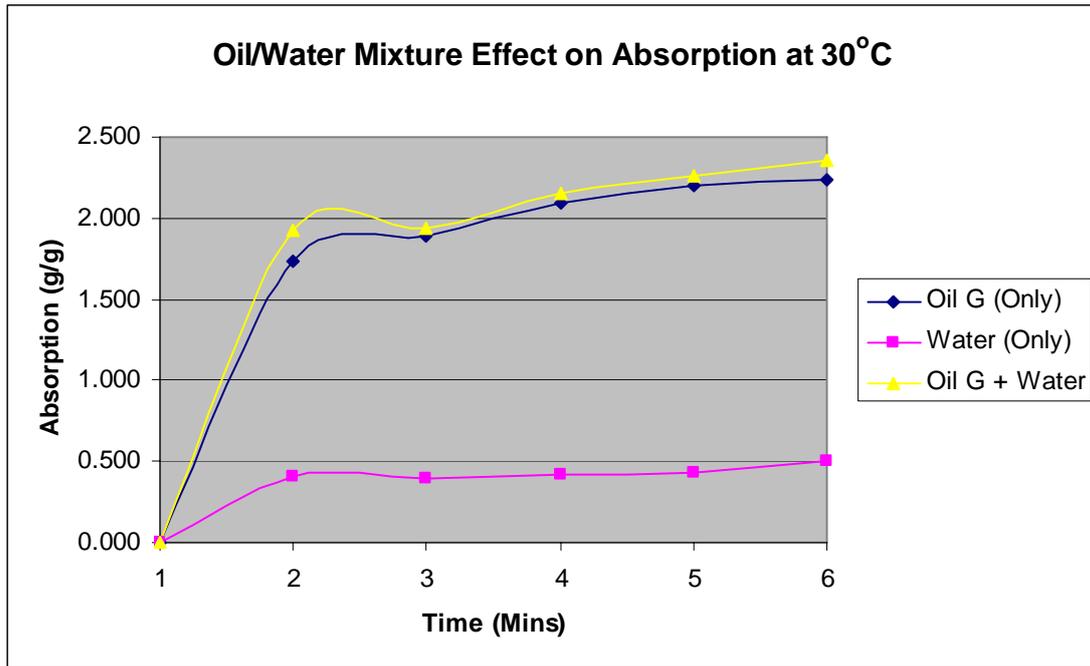


Figure 4.9: Oil/Water Mixture Effect on Absorption

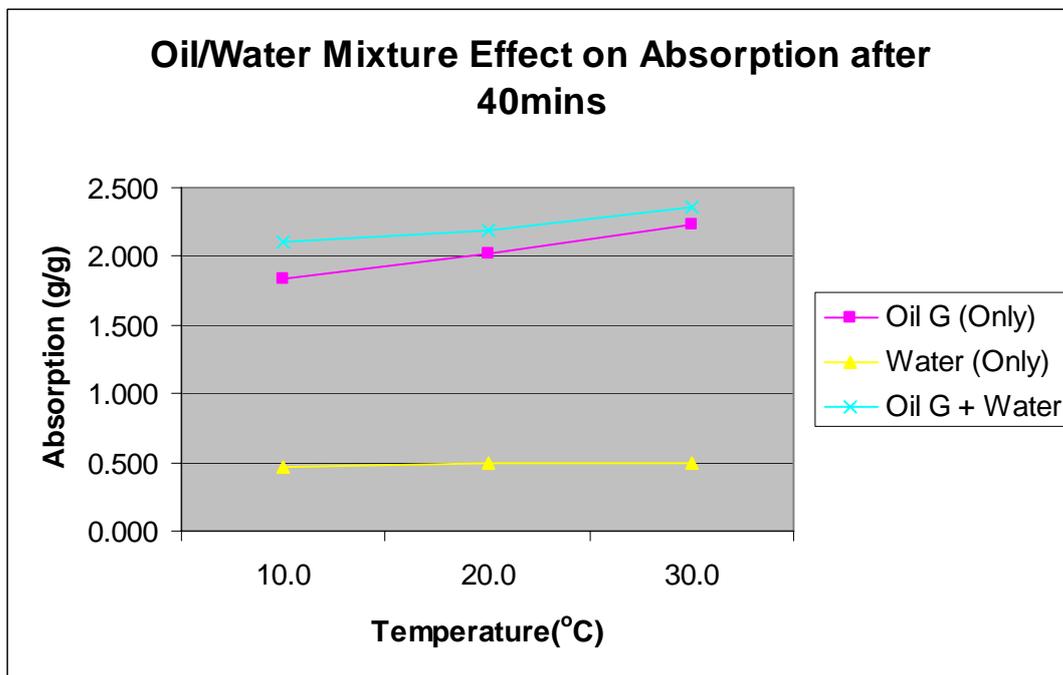


Figure 4.10: Oil/Water Mixture Effect on Absorption after 40mins.

Both figures 4.9 and 4.10 show that water has no significant effect on diesel (Oil G) absorption by granulate. This can be observed from the plots which show the diesel (Oil G) and water absorption curve being very close to oil G only plot. This is further clarified

from the absorption plot of water only on granulate which is observed to be very low. In the experiment water was not absorbed into granulate. The little water absorption seen in the plot is as a result of water retained by wetting of the sieve by water when conducting the experiment.

The result thus shows that the tyre rubber granulate is oleophilic (oil attracting) and hydrophobic (water repelling), which is a desirable property of an absorbent.

Figure A10 and A 11 in the appendix show oil/water mixture effect on absorption at 10°C and 20°C respectively.

4.1.4.5 Exposure Time Effect on Absorption

The absorption studies show an initial rapid increase in absorption rate within the first 5 minutes; it however drops to a much slower rate between 10 to 20 minutes with equilibrium tending to be achieved at about 20 minutes. Increases in mass of absorbed oil after 20 minutes tend to be insignificant within the limits of experimental inaccuracies. It can be said therefore that tyre rubber granulate possibly have quick absorption property.

This could be explained by the fact that oil concentration difference in the granulate acts as the driving force for absorption. The concentration difference is high initially therefore resulting to faster absorption; but this decreases gradually as absorption tends to equilibrium thus lower absorption rate is recorded with time (Aisien, F.A., 2002).

4.2 Environmental Properties Tests

Due to the nature of equipment and standards required to carry out these tests, the samples of tyre rubber granulate were sent to the Technical Research Institute of Sweden (SP), Borås, for the analysis of environmental properties. The following tests were ordered to be conducted on the samples by SP:

- Total Analysis: for metals and organics
- Leaching Test: for metals and organics

4.2.1 Total Chemical Analysis of Granulate

This is testing the granulate for the total content of the following substances

Organics: PAHs, Phthalates, Phenols

Metals: Lead (Pb), Cadmium (Cd), Copper (Cu), Chromium (Cr), Zinc (Zn)

Test for these substances were selected based on literatures reviewed and listing in Basel Convention, 1999; hazardous waste constituent of tyre as well as the Swedish requirement for a non-toxic environment which noted that some of the substances found in tyres are substances of concern (KemI, 2006).

4.2.1.1 Organics Compounds

For analysis of PAHs, phenols, phthalates, about ten grams of the sample is Soxhlet extracted with dichloromethane. The resulting extract was then analysed by gas chromatography/mass spectrometry (GC/MS) and selected ion monitoring mode was used to increase sensibility. The same extraction procedure was used for all the compounds but these required three different injections of the sample in the GC/MS.

4.2.1.2 Metals

For the following metals: Zn, Pb, Cr, Cd in the granulate; EPA method 3051A was used; where about 0,5 g of the sample was dissolved in an acid mixture before warming to 195°C and analysed by inductively coupled plasma - optical emission spectroscopy (ICP-OES).

4.2.2 Chemical Analysis of Granulate Leachate

Analysis of the tyre rubber granulate leachate was by the standard ENV12457-3 (Characterization of waste-leaching-Compliance test for leaching of granular waste materials and sludges). Leaching test was conducted only on 0.5 mm and 2.0 mm granulate samples.

Leaching was performed in two stages. During the first stage, water was added to the sample (around 170g) such that the ratio liquid/solid is 2. The leaching is performed during six hours in a tumbler. The resulting eluate is left to sediment and filtrated to remove all the water. The pH of the eluate is measured.

A part of this water was used to analyse for metals while the rest was extracted with dichloromethane to analyse PAHs, phenol, phthalates with GC/MS.

For the 2nd stage the resulting sample is added water so that the ratio liquid/solid is 10. The leaching is performed during 18 hours in a tumbler.

A part of the water is used to analyse for metals while the rest will be extracted with dichloromethane to analyse PAHs, phenols and phthalates with GC/MS. Evaporation of the extract will be performed in order to lower the detection limit. The pH and the conductivity of the eluate are measured.

The leaching test pH value was 8.

4.2.4 Results and Discussion

Total Chemical Analysis of Granulate

Tables 4.1- 4.3 show results for total chemical analysis of organics; PAHs, phenols and phthalates respectively, in granulate while table 4.4 shows result for metals.

Table 4.1 Total Chemical Analysis for PAHs

PAHs	0,5 mm	1,0 mm	2,0 mm	Swedish Guideline for Polluted Soil
	mg/kg	mg/kg	mg/kg	mg/kg
Naphthalene	2,0	1,8	1,6	
Acenaphthylene	< 0,1	< 0,1	< 0,1	
Acenaphthene	< 0,1	< 0,1	< 0,1	
Fluorene	1,2	1,1	1,0	
Phenanthrene	9,3	10,3	8,1	
Antracene	1,5	1,6	1,2	
Fluorantene	19,0	20,0	15,3	
Pyrene	64,6	67,3	54,6	
Benzo(a)anthracene*	3,6	4,8	2,5	
Chrysene*	8,1	14,6	6,4	
Benzo(b)fluoranthene*	2,1	1,8	1,5	
benzo(k)fluoranthene*	2,6	1,4	1,4	
benzo(a)pyrene*	7,0	7,1	6,8	
Indeno(123cd)pyrene*	< 0,4	< 0,4	< 0,4	
dibenzo(ah)anthracene*	< 0,4	< 0,4	< 0,4	
benzo(ghi)perylene	5,0	5,2	4,8	
Total PAHs₁₆	127,0	138,0	106,2	
Carcinogenic PAHs(Sum of 7)	24.2	30.5	19.4	0.3
Other PAHs(Sum of 9)	102.8	107.5	86.8	20

* Carcinogenic PAHs. (Minnesota Pollution Control Agency (MPCA), 2006)

The result shows that PAHs are present in all the rubber granulates samples tested. It also shows that both the carcinogenic PAHs (sum of 7) and other PAHs (sum of 9) exceeded the Swedish guideline values for levels in polluted soil (EPA, 2002). There is no guideline value for PAHs₁₆. Most PAHs found in tyre are persistent, bioaccumulative and carcinogenic (KemI, 2006).

Table 4.2: Total Chemical Analysis for Phenols

Phenols	0,5 mm	1,0 mm	2,0 mm	Swedish Guideline for Polluted Soil
	mg/kg	mg/kg	mg/kg	mg/kg
4-tert-octylphenol	683,9	685,9	603,4	
4-nonylphenol	< 0,4	< 0,4	< 0,4	

Table 4.3: Total Chemical Analysis for Phthalates

Phthalates	0,5 mm	1,0 mm	2,0 mm
DBP(Dibutylphthalate)	< 5	< 5	< 5
DEP(Diethylphthalate)	< 5	< 5	< 5
DEHP(Diethylhexylphthalate)	14	13	9

Phenols and phthalates were present in all the rubber granulates samples tested; however, no guideline values have been indicated for 4-tert-octylphenol and 4-nonylphenol as well as the Phthalates. These substances have been identified as substances of concern in the Swedish environmental objective for a non-toxic environment. Phenols are persistent and bioaccumulative while phthalates are suspected to affect human reproductive health (KemI, 2006).

Table 4.4 Total Chemical Analysis for Metals

Metals	0,5 mm	1,0 mm	2,0 mm	Swedish Guideline for Polluted Soil
	mg/kg	mg/kg	mg/kg	mg/kg
Zinc(Zn)	3800	2600	2800	350
Lead(Pb)	7,12	4,58	5,67	80
Chromium (Cr)	0,53	0,31	0,59	5
Cadmium (Cd)	0,53	0,36	0,26	0,4
Copper(Cu)*	20	20	70	100

* Values for Copper (Cu) (KemI, 2006).

Analysis of results for total metal content of granules show that values for Pb, Cr, and Cd are below the Swedish guideline for levels in polluted soils for the most sensitive type of land use (except for Cd in 0.5 mm granulate fraction). The literature values for Cu are less than the Swedish guideline but values for Zn exceeded the guideline value.

Chemical Analysis of Granulate Leachate

Tables 4.5 and 4.6 show the results for chemical analysis of granulate leachate for organics; PAHs and phenols respectively while table 4.7 shows the results for metals.

Table 4.5 Chemical Analysis of Leachate for PAHs

PAHs	0,5 mm		2,0 mm		Swedish Guideline for Polluted Ground Water µg/l
	µg/kg	µg/kg	µg/kg	µg/kg	
	LS2	LS10	LS2	LS10	
Naphthalene	< 1	< 4	< 1	< 4	
Acenaphthylene	< 1	< 4	< 1	< 4	
Acenaphthene	< 1	< 4	< 1	< 4	
Fluorene	< 1	< 4	< 1	< 4	
Phenanthrene	< 1	< 4	< 1	< 4	
Antracene	< 1	< 4	< 1	< 4	
Fluorantene	< 1	< 4	< 1	< 4	
Pyrene	< 1	< 4	< 1	< 4	
Benzo(a)anthracene*	< 1	< 4	< 1	< 4	
Chrysene*	< 1	< 4	< 1	< 4	
Benzo(b)fluoranthene*	< 2	< 8	< 2	< 8	
benzo(k)fluoranthene*	< 2	< 8	< 2	< 8	
benzo(a)pyrene*	< 2	< 8	< 2	< 8	
Indeno(123cd)pyrene*	< 4	< 16	< 4	< 16	
dibenzo(ah)anthracene*	< 4	< 16	< 4	< 16	
benzo(ghi)perylene	< 4	< 16	< 4	< 16	
TOTAL PAHs	<28	<112	<28	<112	
Carcinogenic PAHs(Sum of 7)	<16	<64	<16	<64	0.2
Other PAHs(Sum of 9)	<12	<48	<12	<48	10

* Carcinogenic PAHs. (Minnesota, 2006)

Leachate analysis for organics shows the presence of PAHs. There is no guideline value for total PAHs₁₆ in polluted ground water. Measured values for carcinogenic PAHs (sum of 7) and other PAHs (sum of 9) are not clearly defined but is assumed that their values exceed the Swedish guideline for polluted ground water.

Granulate leachate analysis also show the presence of phenols, however no Swedish guideline values have been indicated for 4-tert-octylphenol and 4-nonylphenol. Analysis of phthalates is still in progress.

Table 4.6: Chemical Analysis of Leachate for Phenols

Phenols	0,5 mm	0,5 mm	2,0 mm	2,0 mm	Swedish Guideline for Polluted Ground Water
	µg/kg	µg/kg	µg/kg	µg/kg	µg/l
	LS2	LS10	LS2	LS10	
4-tert-octylphenol	93	284	117	237	
4-nonylphenol	120	149	127	148	

Table 4.7 Chemical Analysis of Leachate for Metals

Organics	0,5 mm	0,5 mm	2,0 mm	2,0 mm	Swedish Guideline for Polluted Ground Water
	µg/kg	µg/kg	µg/kg	µg/kg	µg/l
	L/S 0-2	L/S 0-10	L/S 0-2	L/S 0-10	
Zinc(Zn)	2	4	1	2	30*
Lead(Pb)	<0,1	<0,4	<0,1	<0,4	10
Chromium (Cr)	<0,1	<0,1	<0,1	<0,1	50 ⁺
Cadmium (Cd)	<0,01	<0,01	<0,01	<0,01	5 ⁺
Copper(Cu)**	-	-	-	-	2000 ⁺

*Canadian Water Quality Criteria

⁺ Swedish Limits for Potable Water

** Values were not available for the leaching result for Copper (Cu)

Results of metal analysis show the presence of Zn, Pb, Cr, Cd. The leachate value for Pb was below the Swedish guideline for polluted ground water, limits for potable water as well as Canadian water quality criteria. Like wise the values for Cr and Cd were below the limit for Swedish potable water as well as Canadian water quality criteria. Measured leachate value for Zn was below the Swedish level for Canadian water quality criteria.

It is important to mention that considering the test procedure used in both total analysis and leachate analysis, it will be unrealistic to have such conditions under normal condition of the use of tyre granulate for the desired application as absorbent for oil spill decontamination. Results from absorption tests conducted on the granulate show that it have quick absorption; equilibrium absorption tends to be achieved within 10 to 20 minutes of introduction of granulate with absorption being fastest within the first 5 minutes. This implies that for this application the absorbent will reasonably be used on a contaminated environment for a period not longer than 20 minutes under normal

conditions. This time and condition will be too short for any significant leaching or migration of any substance (if any) to the environment occur. Thus the use of rubber tyre granulate as absorbent for oil decontamination, under normal condition may not pose any significant risk to human health and/or environment.

5. CONCLUSIONS

Based on the reviews conducted, consultations with experts/agencies in the field of oil decontamination and experimental tests conducted with tyre rubber granulate; the following conclusions have been reached:

Most common types of oil spill are small spills. Small spills represent 84% of 10,000 global oil spills incidents on record. Sweden records about 2200 hazardous chemical spills each year; more than half of these spills are small spills which are decontaminated using absorbents. Use of absorbent has been found to be fastest and most suitable method for decontamination of oil spillage particularly small spills. Since small spills are the most common spills, therefore there is an attractive market for absorbents in such applications.

Commonly used absorbents in Sweden are made from materials such as calcium clay or wood bark. Calcium clay materials are not suitable for oil decontamination of natural waters while wood bark has low absorption capacity thus large quantity will be required each time this creates cost and storage problems. Absorbent from tyre rubber granulate overcome these problems because it has higher absorption capacity, it absorbs up to five times its weight in oil. It also can be used in water, on land; indoor and outdoor oil decontamination operations. An added advantage of this material is that it becomes a very good fuel for cement kiln and energy industries after its usage.

Absorption tests conducted in the laboratory to test the absorption ability of tyre rubber granulate on different types of oil [gasoline (E95), diesel, Inboard Oil (15W-40) Shell Helix Plus (10W-40), Shell Helix Ultra (5W-40)] show that tyre rubber granulates upon contact with the oil experiences an increase in size due to oil absorption. It demonstrated the intrinsic property of rubber granulate to absorb organic compounds.

Analysis of the absorption capacity of tyre granulate show that exposure time, granulate particle size, temperature and type of oil absorbed have effect on the absorption ability of granulate; the presence of water however, was found not to have any significant effect on oil absorption, which implies that granulate can be used for oil decontamination in sea and water bodies.

Tyre granulate has quick absorption capacity; its absorption rate was found to be fastest within 5 minutes of exposure and tends to achieve equilibrium absorption at about 20 minutes. It was also observed that absorption ability of tyre rubber granulate increases with decrease in particle size and increase in temperature with the highest absorption observed when the smallest particle size, 0.50 mm was used at 30°C. Viscosity and probably the chemical composition of the oil also affect the amount of oil absorbed. Absorption was found to increase with decrease in viscosity of the oils. The highest absorption 2.518 g/g was recorded with the least viscous oil; gasoline.

Environmental property tests conducted at the Swedish Technical Research Institute (SP) show the presence of PAHs, phenols and phthalates in tyre rubber granulate. PAHs composition of granulate and in the leachate exceeded the limit value for Swedish guideline on polluted soil and polluted ground water respectively. Granulate composition

of all metals tested (Cd, Cr and Pb) were below the Swedish guideline values for polluted soil with exception of zinc; however all the metal found in the leachate were below the available guideline values for polluted ground water.

The concern that the chemical composition of tyre rubber granulate could be of environment concern poses no treat. This is because tyre rubber granulate is a quick absorbent thus will be used on the contaminated site for a very short time; within 20 minutes. This time is too short for any contamination of environment by tyre rubber constituents to occur (if it ever occurs) since emission, leaching or migration of granulate constituents occur under extreme conditions which cannot be obtained during real application of the tyre rubber granulate for oil decontamination.

To further solve the problem of tyre composition, Sweden has been working actively within the EU to prohibit high aromatic oils in tyres. The EU decided in the summer of 2005 to introduce limits for the concentrations of PAHs in newly manufactured tyres. The new regulations will come into force in 1st January, 2010. This will in the long term lead to lower levels of PAHs in the rubber from recycled tyres. Hence making recycled tyres more environmental friendly for products development including absorption mats.

Conclusively, tyre rubber granulate has demonstrated an intrinsic ability to absorb organic compounds in this case oils; it can therefore be developed into absorption mats for oil spill decontamination. There is very good market for absorbents in oil spill decontamination particularly absorbents made from tyre rubber granulate which will find application at any location of the spill. The unique aspect of absorption mats from tyre rubber granulate is that it an innovative way of managing end-of-life tyres as well as cleaning our environment of oil spill. This material will also be a very valuable energy source after use. Finally, the use of tyre rubber granules for oil decontamination will not pose any health and/or environment risk when used adequately.

6. FURTHER WORK

It is recommended that further work in this research should go deeper into the development of the absorption mat prototype. Based on consultations with experts in the rubber industry; it is suggested that prototype research should be conducted as follows:

- Prototypes should be produced using three types of binders (polyurethane, rubber latex and rubber reclaim) or any additional one that might be identified.
- Each binder type should also be used to produce the mats in all the different shapes being considered.
- The produced absorption mat prototypes should then be evaluated in terms of
 - ✓ Absorption capacity
 - ✓ Cost of manufacture process
 - ✓ Ease of manufacture process
 - ✓ Disposal route

Based on those, the most efficient method and shape may be developed for commercialization.

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APPENDIX



Figure A1: Mechanical Shaker for granulate separation into fractions

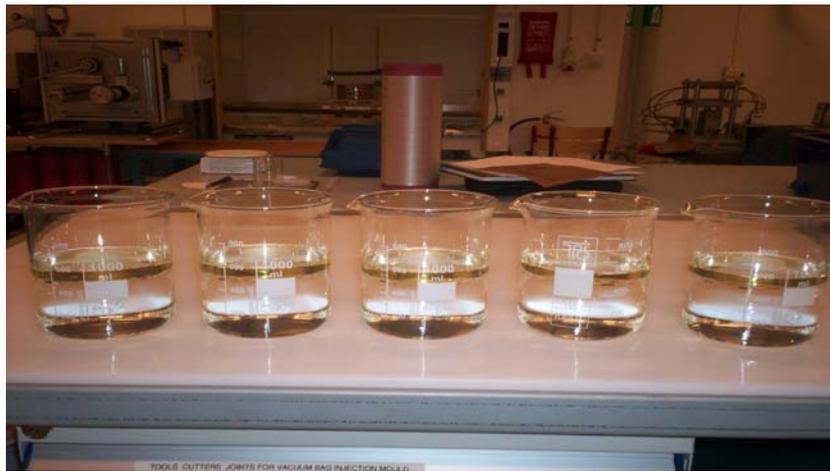


Figure A2: Oil/Water Mixture before Absorption Studies



Figure A3: Experimental Set-Up for Absorption Studies

Table A1: Absorption Test Experiments Conducted On Tyre Rubber Granulate

Oil Type	Temperature (°C)	Granulate Size (mm)	No. of Experiments
SUPER GOLD: 15W-40 (Oil A)	35	1.0	1
	30	0.5 1.0 2.0	3
	25	0.5 1.0 2.0	3
	20	1.0	1
INBOARD OIL: 15W-40 (Oil C)	30	1.0 2.0	2
	20	1.0 2.0	2
	10	1.0 2.0	2
SHELL HELIX PLUS DIESEL: 10W-40 (Oil D)	30	1.0 2.0	2
	20	1.0 2.0	2
	10	1.0 2.0	2
SHELL HELIX ULTRA 5W-40 (Oil E)	30	1.0 2.0	2
	20	1.0 2.0	2
	10	1.0 2.0	2
GASOLINE E95 (Oil F)	30	1.0	1
	20	1.0	1
	10	1.0	1
DIESEL (Oil G)	30	1.0	1
	20	1.0	1

	10	1.0	1
DIESEL + WATER	30	1.0	1
	20	1.0	1
	10	1.0	1
WATER (Only)	30	1.0	1
	20	1.0	1
	10	1.0	1
TOTAL			38

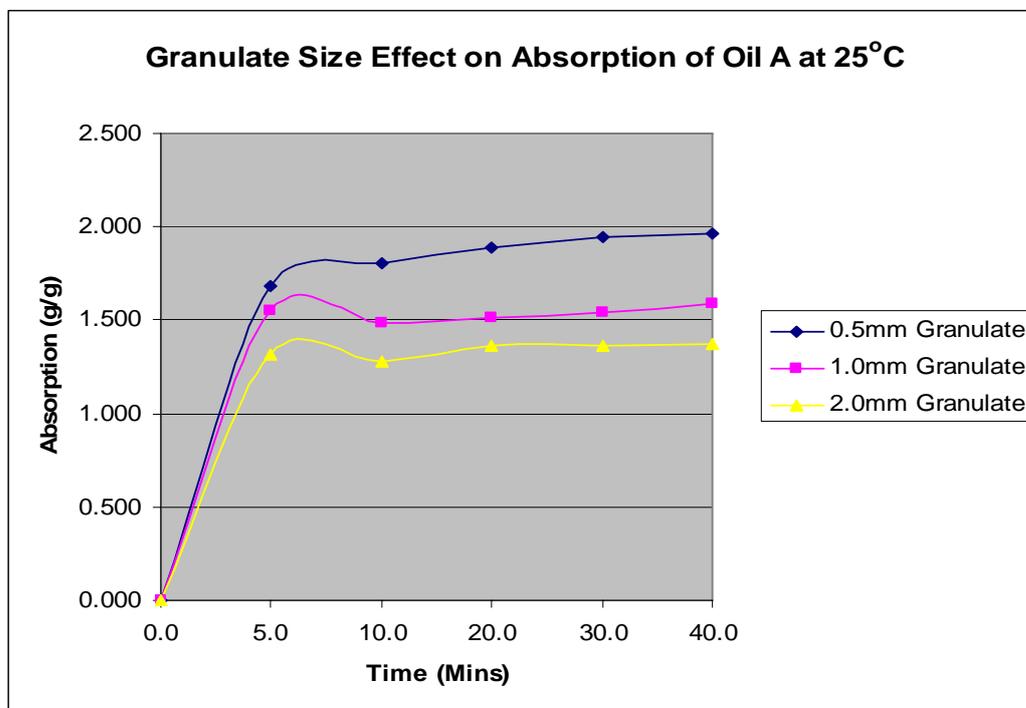


Figure A4: Granulate Size Effect on Absorption of Oil A at 25°C

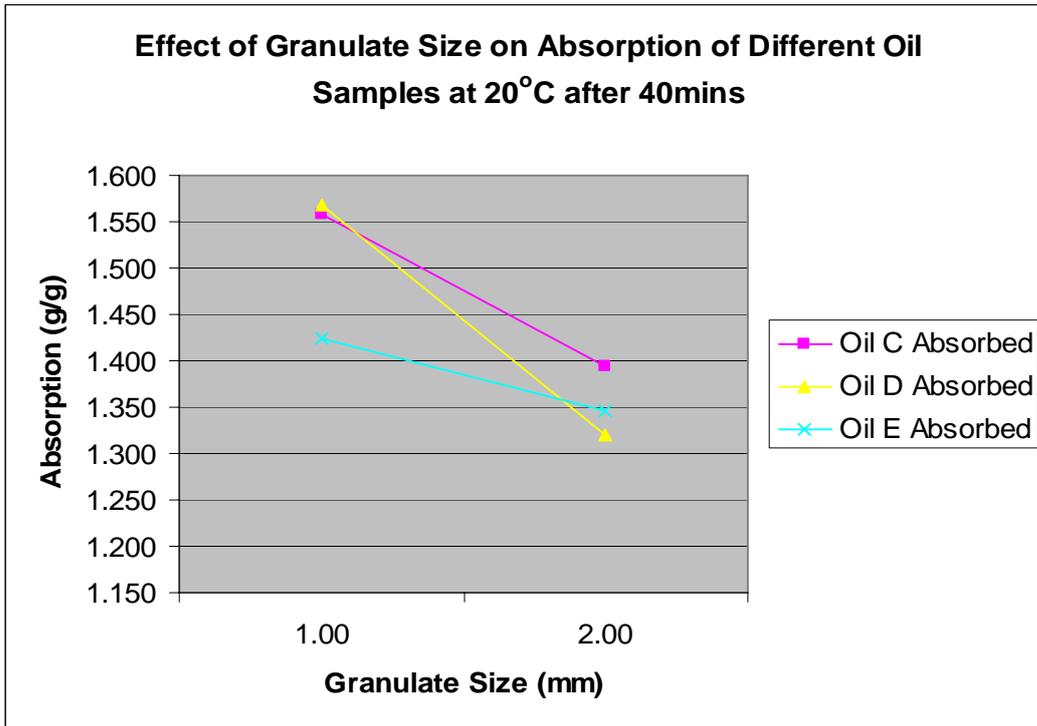


Figure A5: Granulate Size Effect on Absorption of Different Oil Samples at 20°C

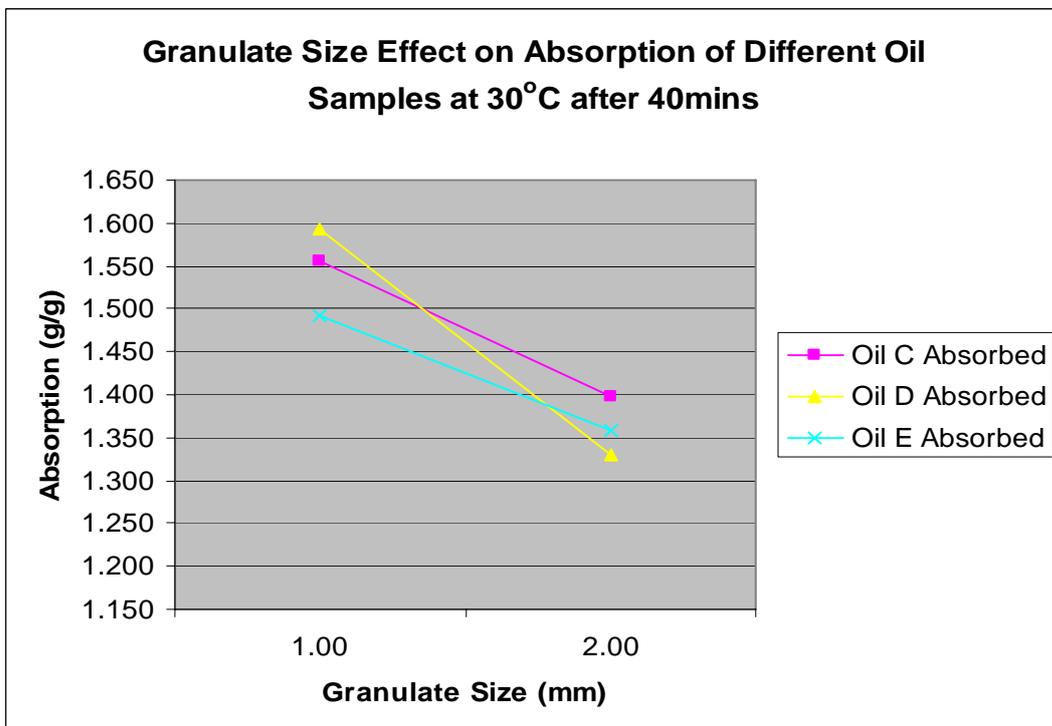


Figure A6: Granulate Size Effect on Absorption of Different Oil Samples at 30°C

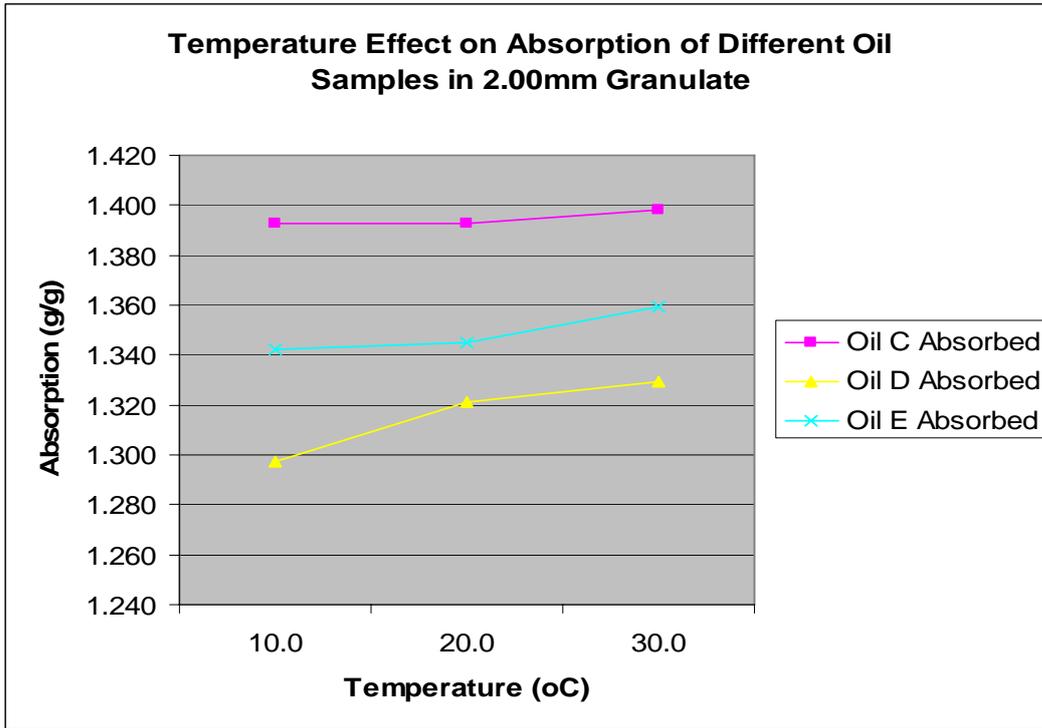


Figure A7: Temperature Effect on Absorption of Different Oil in 2.00mm Granulate

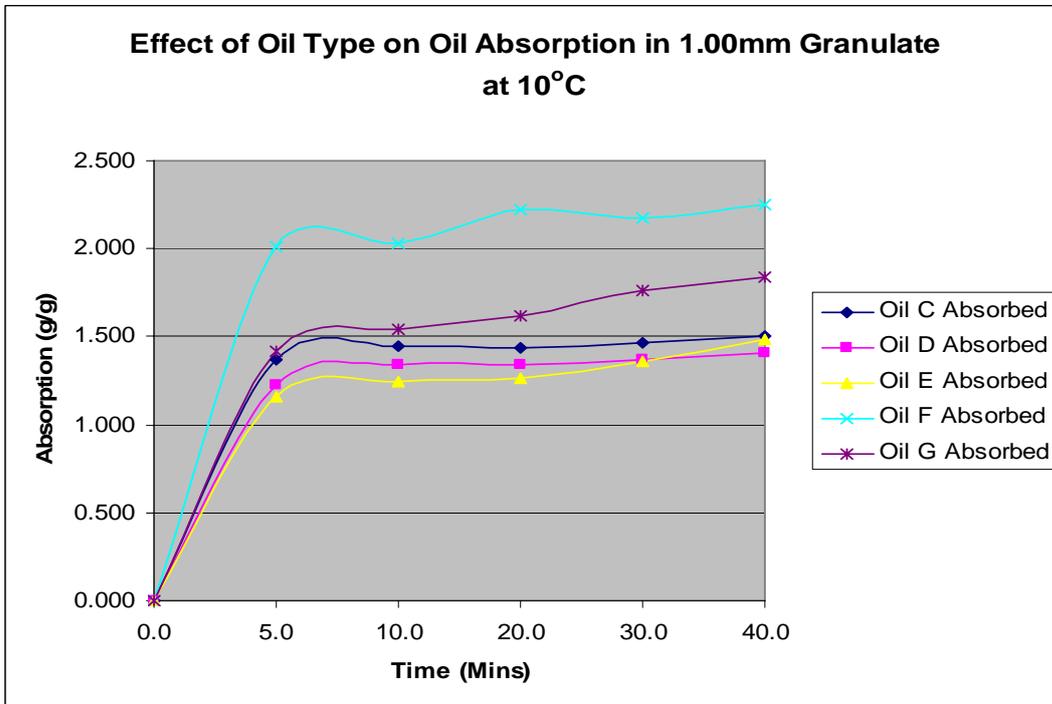


Figure A8: Oil Type Effect on Oil Absorption at 10°C

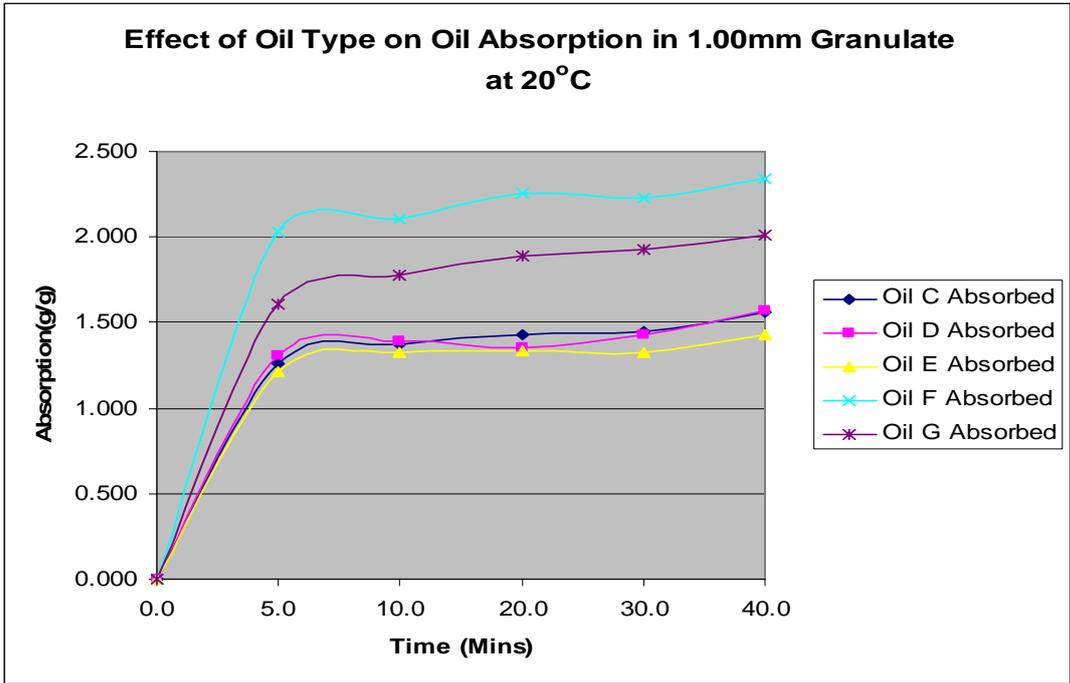


Figure A9: Oil Type Effect on Oil Absorption at 20°C

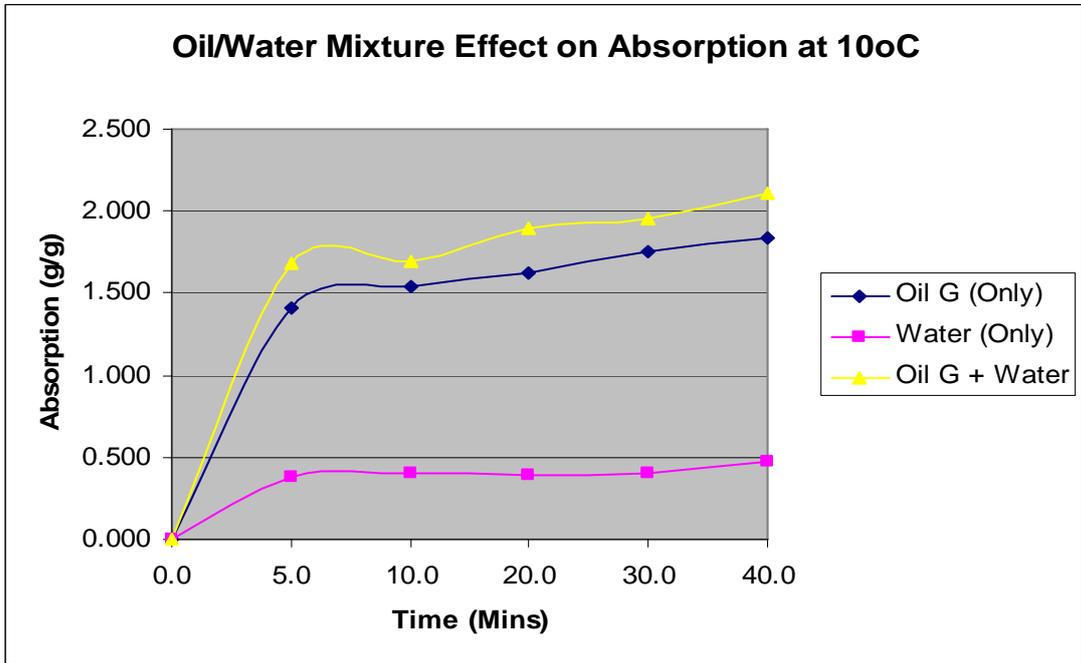


Figure A10: Oil/Mixture Effect on Absorption at 10°C

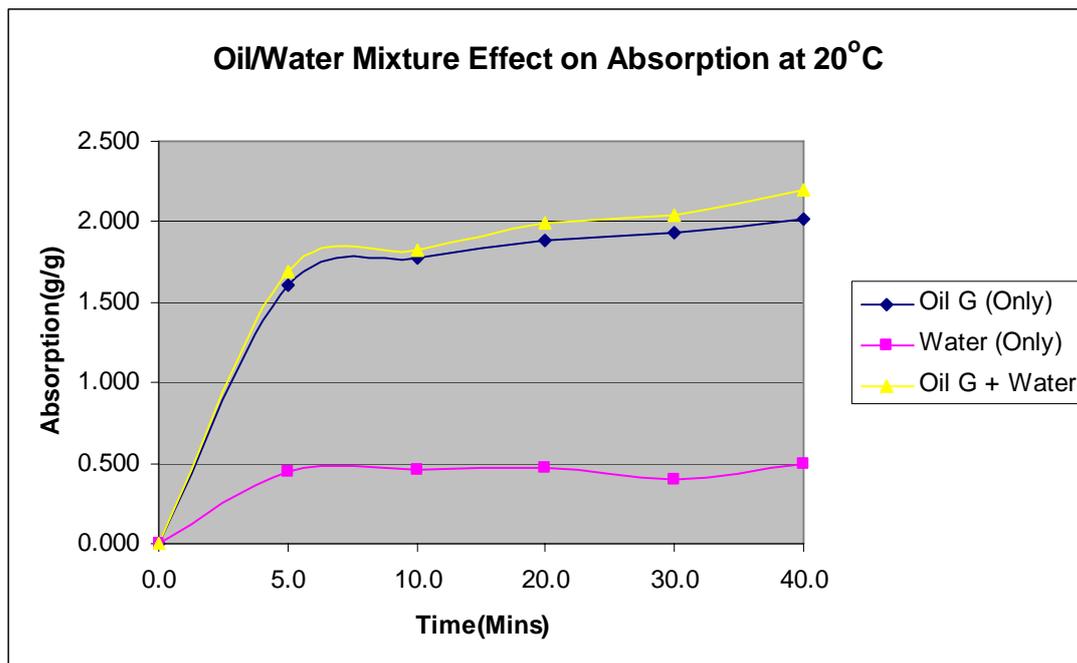


Figure A11: Oil/Mixture Effect on Absorption at 20°C