

**DESTRUCTION OF POLYCYCLIC AROMATIC
HYDROCARBONS (PAH's) AND ALIPHATIC
HYDROCARBONS IN SOIL USING BALL MILLING**

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Statement of originality

‘I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the qualification of any other degree or diploma of a university or other institution of higher learning, except where due acknowledgment is made in the acknowledgments’

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ABSTRACT

This study involves the use of ball mill as a mechanochemical reactor in the destruction of environmental contaminants. Although the technology has the potential to be used for a wide range of organic contaminants, this study focused on polycyclic aromatic hydrocarbons (PAH's) and aliphatic hydrocarbons.

There are different methods for the remediation of the environmental contaminants such as biological, chemical and thermal techniques, most of which are costly. The ball mill is less costly as it involves low technology and little or no other chemicals seem to be needed to give complete destruction of the substances investigated. The mill is relatively easy to construct and can be made in different designs and dimensions to fit its intended purpose i.e. they can range from a laboratory scale to a very large industrial mill for the continuous processing of tonnes of material at a time. The process can be sealed so pollution from the mill is easy to control.

In this study two classes of environmental contaminants were investigated. PAH's are common byproducts of combustion and are found as contaminants in many soils. The other compounds investigated were the larger aliphatic hydrocarbons. These were chosen as being representative of the evaporated residues from fuel spills or leaks.

A laboratory scale centrifugal ball mill with capacity of approximately 200 g was used for the study. The PAH's investigated were naphthalene, anthracene and phenanthrene. The aliphatic hydrocarbons n-eicosane and n-octacosane were used as the model compounds for hydrocarbon residues. Different soil types (scoria, clay soil, silica sand and slag) were spiked with a known amount of these contaminants. The ball milling was done under different milling conditions i.e. with different ball ratio and with different milling duration. In some experiments there was an addition of materials such as a potential free radical trap or metals to investigate the effect on the mechanochemical reaction.

The samples were analysed using an ultrasonic extraction method (EPA METHOD 3550C) with GC and GC-MS analysis of the extract for the quantification of the residual contaminant in the soil and identification of possible secondary products and reaction intermediates.

It was found that high destruction efficiency was achieved using milling times of between 120 and 150 minutes and high ball to soil ratios for example 7:1 ball mass to soil mass ratio. Also it was found that different type of soil had an influence on the mechanochemical reaction. A silica matrix was found to have a better destruction rate compared to scoria and clay soil. It was also found that the PAH compounds were more rapidly destroyed by ball milling than were aliphatic hydrocarbons.

The addition of BHT was found to reduce destruction rate of both PAH's and aliphatic hydrocarbons. This suggests the mechanism of destruction may involve a free radical mechanism. Aluminium metal was observed to have no significant effect in the destruction. The presence of lubricants such as waxes in the contaminated soil appeared to inhibit the mechanochemical reaction although the mechanism is still uncertain.

From this study it was concluded that, the ball mill has considerable potential as an effective, low cost method for the destruction of certain environmental contaminants.

CHAPTER 1

1.0 INTRODUCTION

1.1 BACKGROUND

There are number of issues that have a significant impact on the environment. For example, the displacement of native plants, erosion, chemical contaminants and other environmental aspects of agriculture have enormous potential for environmental damage (1). Soil erosion has an immediate on-site effect which involves removal of top fertile soil. However, soil erosion also has off-site effects. Sediments can clog waterways but less obviously, agricultural chemicals, such as pesticides and fertilizer that are often move with eroded sediments. These chemical move into, and pollute or contaminate downstream water sources and recreational areas (2).

Chemical contamination of agricultural products used for human consumption can be caused by a variety of human activities. The main problem is that any agricultural chemicals used on the land have a potential to contaminate it in some way (3). The range of human activities that will eventually end in the contamination of land and thereafter the agricultural products is broad.

Environmental contamination by substances such as hydrocarbons (oil spills, waste), pesticides (crop treatment), heavy metals and various other organic pollutants (examples are aromatic hydrocarbons, ethers etc) and waste waters is a major environmental concern world wide (4). Environmental pollution problems are often only belatedly recognized because their damage takes years to be noted (5). Pollution damages both the environment and can seriously affect the lives and health of human beings. It is clear that an effort must be made to reverse this trend.

Polycyclic aromatic hydrocarbons (PAH's) are a class aromatic compounds and are pervasive organic pollutants. PAH's are an important group due to their widespread distribution in the environment and their carcinogenicity (6). The main sources of

PAH's are incomplete combustion, diagenetic processing of organic matter, and to a smaller extent, forest fires and microbiological synthesis or transformations. PAH's are often found on contaminated sites, particularly in connection with coal tar contamination at former gasworks, they also exist as diffuse contamination in urban areas and alongside roads, and in few cases, PAH's have been found in connection with oil pollution (6). Environmental contamination of soils with PAH's generally involves mixtures of these compounds.

Persistence of hazardous pollutants in the environment is due to the stability of their molecular structures (7). There are various remediation techniques which have been employed in the removal of environmental pollutants such as biological and thermal treatments as discussed in the literature part, however, the costs of these methods are high. An example is thermal treatment by using high temperature incineration (8). Effective destruction or minimization of toxic hydrocarbon species can be found only at the highest temperature and longest residence times explored (1150°C and 2seconds). This means incinerators have high operating costs due to high operating temperature and design constraints.

These difficulties of environmental stability and high cost of destruction methodology can be effectively overcome by mechanical activation of mechanochemistry reaction inside a *ball mill*. Chemistry occurring at surfaces under impact has been investigated for a long time and has found numerous practical applications. This leads to two branches of chemistry, i.e. mechanochemistry and/or tribochemistry. Mechanochemistry deals with the chemical and physico-chemical changes of substances of all states of aggregation due to mechanical energy while tribochemistry deals with chemical and physico-chemical changes of solids due to the influence of mechanical energy (7). Use of ball mills will reduce the remediation cost because mechanochemical degradation can be performed at low temperature in many cases less than 100°C (7) and no harmful emissions to the environment are expected by using ball mill as a mechanochemical reactor.

In this study the focus was on two significant pollutants, PAH's and hydrocarbon fuel residues.

1.2 A BRIEF DISCUSSION ON ENVIRONMENTAL POLLUTANTS THAT HAVE A DEMONSTRATED POTENTIAL TO BE DESTROYED USING BALL MILLING

i) Polycyclic Aromatic Hydrocarbons (PAH's)

PAH's constitute a family of hazardous compounds that are widely present as contaminants in the environment. PAH's have been detected in exhaust gases, smoke, airborne particles surface and drinking waters, soils and sediments (9). They are common constituent of fuels and used lubricating oils. Generally, sources of PAH are soot particles containing combustion related PAH's mostly arising from internal combustion engines, especially diesel engines. Street run-off containing traces of burnt fuels, used lubricating oil and hydraulic oils, has a complex profile with higher molecular weight PAH's (4 to 6 rings) (10).

PAH's, in particular (11): naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, Acenaphthene, 2-Ethylnaphthalene, Fluorene, Phenanthrene, Anthracene, Fluoranthrene and Pyrene are found to be a problem in the soil. PAH's are known to be strongly adsorbed to soil particles, and some are carcinogens. PAH induced carcinogenesis involves number of steps including; (i) the enzymatic activation of the PAH into metabolites; (ii) the covalent binding of the PAH metabolites to DNA; and (iii) the induction of mutations that serve to initiate the transformation process as a result of PAH-DNA adducts.

It has been found that the higher molecular weight PAH's, such as chrysene, pyrene, and benzo[a]pyrene, especially, exhibit low bioavailability characteristics because of their very low water solubility therefore light PAH's bioaccumulate more easily than heavy PAH's. PAH's with fewer fused rings will volatilize more easily and biodegrade more quickly (12, 13).

PAH's can also be spread by the ashes from the incineration process of combustible waste. They are the organic compounds that are known to be present in ashes. They are

formed during incomplete combustion of organic materials (14). Different sources of ash have been observed to have different levels and patterns of PAH's.

It was found (14) that naphthalene and phenanthrene were the dominant individual PAH's from the ashes taken from municipal solid waste incineration (bottom ash). Total amounts of PAH analysed were between 480 and 3590 µg/kg. While the total amounts of PAH's in the ash from the mixed biofuel (fly ash from paper mill and bottom ash from the incineration of biofuels in heating plant) were between 57,800 and 77,100 µg/kg. Again naphthalene and phenanthrene were most abundant. Also, the percentage of carcinogenic PAH's varies between different ashes (14). The PAH's considered most carcinogenic are; benzo(a)pyrene, benzo(a)anthracene and benzo(a)fluoranthene.

Anthracene and phenanthrene are considered prototypic PAH's and serve as signature compounds to detect PAH contamination, since their chemical structures are found in carcinogenic PAH's. They have also been used as model PAH's to determine factors that affect the bioavailability, biodegradation potential, and rate of microbial degradation of PAH's in the environment (15).

The pattern and level of PAH's varies not only in ashes but also in other different areas such as in the soil. It was found in forest soils (organic horizons) (16) that the sum of PAH concentrations increased going down through the organic horizons.

Studies like this show that the analysis of PAH's in soil is complex since the level of contamination in the soil differs with the type of soil as well as type of PAH even though they are from the same source of contamination as observed in PAH's analysis of ashes.

Furthermore, there are factors which may influence the mobility of PAH's. A study using naphthalene showed that the following all have an effect on naphthalene level including, naturally occurring soil organic matter (SOM), xenobiotic organic matter (XOM) and other PAH molecules present in the medium under various physical states. According to the study conducted by Bayard *et al*, (17) the presence of other PAH's

had no effect on naphthalene sorption to soil when present in the aqueous solution or as undissolved solids, due to their low solubility in water.

Adsorbed phenanthrene was found to reduce naphthalene sorption (17) only when present at relatively high concentrations of about 120 mg/kg in the soil. Moreover, naphthalene sorption appeared to be proportional to the amount of coal tar (XOM) added to the sand or soil, and a much higher affinity of naphthalene for XOM than SOM was observed. Around 90% of naphthalene retention was found to occur within the organic phase, suggesting a phase partition process which may be explained by the amorphous nature of the XOM and its extreme affinity for naphthalene. In the case of SOM, which is present as porous microaggregates of clay and humic substances, with less affinity for naphthalene, only 1/3 of the naphthalene retention was found to occur within the organic phase, underlining the significant role of surface adsorption in the short term behaviour of naphthalene in soil (17).

Due to their toxicity, mutagenicity and/or carcinogenicity, low solubility, hydrophobic and lipophilic properties, PAH's in the environment can be easily bio-accumulated to an extent that threatens the safety of food chain for both man and animals (18). When these complex mixtures of hazardous chemicals such as PAH's contaminate the food supply of animals, they become more concentrated as they move up through the food chain. They can have severe and long-lasting effects on health.

PAH contamination is not necessarily associated with obvious industrial activity. As a local example, in Auckland city there is a case of soil contaminated by both metals and PAH's (19). The Edenvale Reserve in Mt. Eden has been found to have measurable concentrations of PAH's, including benzo(a)pyrene. The risk to park users is considered negligible because the entire park is covered by grass. However there is a risk to small children who have the habit of eating non-nutritional substances such as soil and other dirt contaminated objects (19). This indicates the importance of doing soil testing based on previous land use.

Toxicological effects of PAH's

Humans exposed to complex mixtures of PAH have shown to have increased rates of lung, skin and breast cancer. Understanding the mechanisms of carcinogenesis by complex mixtures of PAH is difficult since humans generally undergo long-term exposure to low levels of PAH's. Metabolism of the PAH's occurs primarily via oxidation by the cytochrome P450 isozymes to an epoxide, which is hydrolysed to a diol by epoxide hydrolase and oxidised on the same ring by cytochrome P450 to produce a diol epoxide. It is known that PAH can covalently bind to DNA, RNA and proteins, but it is the amount of covalent interaction between PAH's and DNA that correlates best with carcinogenicity (11).

Additionally, there are a number of factors which affect the PAH tumor initiation process. The structure of the PAH molecule can play an influential role. The basic structures thought to be involved in determining the carcinogenicity of PAH are a bay-region and fjord-(hindered-bay) region (Figure 1.1). The fjord-region causes repulsive interactions between two opposing hydrogen bonds in this region, distorting the molecule and rendering it out-of-plane. Some fjord-region containing PAH have been found to bind more extensively to DNA and thus render a greater tumorigenic response (11).

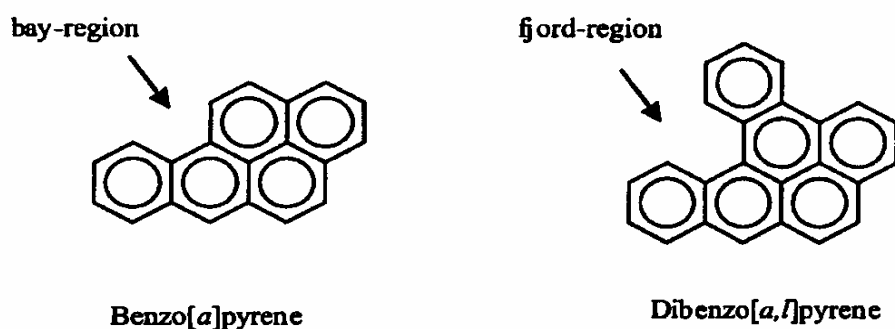


Figure 1.1: Bay region and fjord region of PAH's

Several classes of environmental contaminants have been suspected to possess endocrine-disrupting potency, which may result in reproductive problems and

developmental disorders. Also there is evidence which suggests that mixtures of PAH directly interfere with the thyroid gland, with thyroid hormone metabolizing enzymes, such as uridine-diphosphate-glucuronyl transferases, iodothyronine deiodinases and sulfotransferases in liver and brain; and with the plasma transport system of thyroid hormones in experimental animals and their offspring (20).

ii) Agricultural chemicals

There are different range of contaminants of the agricultural products due to their presence in the soil and underground water. The most significant of these chemicals are referred to as Persistent Organic Pollutants (POPs). POPs are organic compounds that resist photolytic, chemical and biological degradation. They are characterized by low water solubility and high lipid solubility, resulting in bioaccumulation in fatty tissues of living organisms. They are semi-volatile, enabling them to move long distances in the atmosphere, resulting in wide-spread distribution across the earth, including regions where they have never been used. POPs are also transported in the environment in low concentrations by movement of fresh and marine waters. Thus, both humans and environmental organisms are exposed to POPs around the world, in many cases for extended periods of time.

The twelve specified POPs covered by the Stockholm Convention are (21): Pesticides: aldrin, chlordane, dieldrin, dichloro-diphenyl-trichloro-ethane (DDT), endrin, heptachlor, hexachlorobenzene, mirex, toxaphene. Industrial Chemicals: Polychlorinated biphenyls (PCB), Trichloroethane, Chloroform, Pentachlorophenol (PCP).

When the chlorinated pesticides are burned or heated to high temperatures a number of hazardous by products including Dioxins and Furans are formed (refer to section 1.3.2).

The following are the examples of activities and chemicals used which have caused problems in our environment world wide.

One of the activities involved is the application of pesticides and fertilizers to cropland. The term pesticide is applied to literally thousands of different, specific chemical-end products. Pesticides include insecticides, fungicides, herbicides, acaricides, nematocides, and rodenticides. All these can lead to contamination of the land. However the greatest concern is those which exhibit persistence properties, for example organochlorine compounds such as DDT. Although this chemical is no longer used but is still a problem in our environment due to its persistence.

Another activity in countries like New Zealand where livestock is routinely treated against infestation of the animals by parasites is the residues from the treatment process. In New Zealand, from about 1850 sheep have been dipped in solutions of insecticide to protect against keds, ticks, lice and fly-strike. Between 1908 and 1993, annual sheep dipping or spraying was compulsory under various Acts of Parliament (22).

Sheep dip chemicals were arsenic-based until the 1950s, with organochlorine (e.g. dieldrin, lindane and DDT) and organophosphate (e.g. diazinon) insecticides used after this. More recently, synthetic pyrethroids and insect growth regulators (IGRs) have been used. Fortunately these recent pesticides are generally more biodegradable.

Sheep dips (which were often simply a hole in the ground) were usually emptied into nearby creeks or directly onto surrounding soil, also spillage and splashes of these chemicals have left toxic residues in soil, wet sheep standing in a holding paddock have also contaminated the soil. Some of these chemicals persist in the soil for many years. Arsenic does not degrade or break down over time at all. Research shows that the half-life of dieldrin the most commonly used pesticides is about three years thus, many sites in New Zealand still have significant levels of dieldrin, and are a threat to the environment and public health (23).

Sheep dip chemicals may also leach into groundwater. In sampling studies at former sheep dip sites in Canterbury, pesticide concentrations of up to 4,390 mg/kg were recorded. All of the sites that were sampled in the Canterbury study had some results that exceeded the soil acceptance value for arsenic indicating that contamination from dip and bath sites must not be ignored. Results that exceed the soil acceptance values

are relevant in situations where the contaminated soil may come into contact with people or the environment. This may occur in situations where people plan to live on or near the old dip or bath site, when livestock grazes or crops are grown in that area, or when drinking water is obtained from groundwater in the vicinity of the dip/bath site. Although only arsenic was included in the Canterbury sampling studies, it is anticipated that other chemicals used for dipping sheep at these sites, such as dieldrin and lindane, will also be present (23).

People exposed over a long period of time to arsenic and other insecticides like dieldrin and lindane (for example, through drinking contaminated water, skin contact with contaminated soil, eating food grown in contaminated soil) may not become immediately sick, but over a lifetime may be predisposed to cancer and other serious illnesses. Stock exposed to toxic chemicals may become sick in the same way, and meat and dairy products may contain pesticide residues that could limit their sale especially to export markets. In general many of the chemicals that have been used in sheep dips are hazardous to humans, animals and the wider environment (22).

iii) Polychlorinated biphenyls (PCB's)

Another class of chemicals known to contaminate the environment are the PCB's. They are synthetic organic chemicals that are to a large degree chemically inert. PCB's have been widely used in the electrical supply industry from the 1930s, mainly in transformers and capacitors. In the past, PCB's were also used as heat exchange fluids, in hydraulic machinery, as paint additives, in carbonless copy paper and in plastics. The use of PCB's has been illegal in New Zealand since 1994, and most stocks have now been shipped overseas for destruction (24).

Although the chemical stability of many PCB's has been a benefit from the standpoint of commercial use, it has created an environmental problem because it translates into extreme persistence when the PCB's are eventually released into the environment. In fact it has been reported (21) that, the PCB's are among the most widespread environmental pollutants having been detected in virtually all environmental media. They are found in many different geographic locations in air, water, and soil, in almost

every corner of the globe. PCB's can be toxic to exposed human, in part because they bioaccumulate in the food chain. PCB's were produced on an industrial scale for more than fifty years and had been exported as chemicals and in products to virtually every country in the world. Countries that manufactured PCB's include Austria, China, Czechoslovakia, France, Germany, Italy, Japan, the Russia Federation, Spain, the United Kingdom and the United States (21).

PCB's can be released into the general environment from poorly maintained toxic waste sites, by illegal or improper dumping of PCB's wastes, such as transformer fluids, through leaks or fugitive emissions from electrical transformers containing PCB's, and by disposal of PCB-containing consumer products in municipal landfills (25). Once released into the environment, PCB's adsorb strongly to soil and sediment.

Toxicological effects of PCB's

PCB's are primarily metabolized in the liver, therefore persons with impaired hepatic function might be at increased risk because of their diminished ability to detoxify and excrete these compounds. However, PCB's are only slowly metabolized and excreted. The slow metabolism of PCB's leads to bioaccumulation even at low exposure level. After PCB's are absorbed into the body, they are firstly distributed into the liver and muscle tissue, then subsequently to the adipose tissue, skin and other fat-containing organs (25). In dermatological studies, PCB's have been associated with formation of chloracne. The acneform lesions arise as a result of inflammatory responses to irritants in the sebaceous glands (25).

Epidemiologic investigations have shown that, reproductive function can be disrupted by exposure to PCB's. This can cause neurobehavioral and developmental deficits in newborns exposed to PCB's in utero, and these defects continue in older children (25). PCB's have also been identified as possible environmental endocrine modulators (chemical that mimic or disrupt the action of naturally occurring hormones). In the Dutch population, elevated PCB levels correlated with lower maternal levels of circulating triiodothyronine and total thyroxine. Since thyroid hormones are essential for normal behavioural, intellectual, and neurologic development, it is possible that the

deficits in learning, memory, and attentional processes observed in the offspring of PCB-exposed women are partially or predominantly mediated by alterations in hormonal binding to the thyroid hormone receptor (25).

It is also known that, exposure to PCB's can increase serum levels of hepatic enzymes and can induce microsomal enzyme function. At present, the weight of evidence from human studies does not support a causal association between PCB's and human cancer (25), but epidemiological studies have raised concerns about the potential carcinogenicity of PCB's, because the results showed that exposed workers had increased incidences of malignant melanoma and cancers of the liver, gall bladder, and brain. It is also proposed that the PCB's may induce breast cancer, however, the results of epidemiologic studies in PCB's exposed women have been inconsistent (25). The Department of Health and Human Services (1991) has determined that PCB's may reasonably be anticipated to be carcinogens. This is based on animal studies. Studies in workers directly exposed to PCB's do not provide enough information to show with any certainty that PCB's cause cancer in humans (26).

Although PCB's were not investigated in this research, it is expected that, based on the similarity of their chemical structures to the PAH and aliphatic hydrocarbons compounds investigated in this thesis, PCB's will also be readily destroyed in the ball milling process. All chlorinated aromatics can probably be destroyed (7, 27, 28, 29).

iv) Pentachlorophenol (PCP)

PCP is a chlorinated aromatic organic chemical with low volatility. It is a contaminant found at many wood-preserving sites since it has been used mainly as wood preservative. Because treated (preserved) wood is generally used in locations exposed to the environment and because such structures are intended for long term use, PCP and its associated contaminated soil can be found in many places and represents an ongoing problem. PCP may also be released to the environment as a result of its manufacture, storage and transportation. It was banned in 1987(EPA) (30). PCP does not decompose when heated to its boiling point for extended periods of time.

PCP has both noncarcinogenic and carcinogenic health effects. PCP is a proven carcinogen in rodent studies and there is some epidemiological evidence that PCP is carcinogenic in humans (30).

Toxicological effects of PCP

Various studies of PCP showed acute toxicity and chronic toxicity, reproductive effects, teratogenic effects, weak mutagenic effects, carcinogenic effects, organ toxicity (liver, kidney) and central nervous system problems (30).

v) Fuel Hydrocarbons

A common hazardous activity or industry that we have information on is the storage of hazardous substances in underground storage tanks. For example fuel (petrol and diesel) service stations will have underground fuel storage tanks. These tanks need replacing with age, or may be removed when a service station closes or changes ownership. When tanks are removed, an environmental assessment of the soils in the tank pit enables any contamination problems that have arisen during the working life of the tank needs to be identified and managed.

In some countries, underground storage tank systems are considered as a major source of ground water and soil contamination due to the potential for the undetected leakage of product to the environment. Some of the many features associated with underground storage tanks that can fail are the storage tanks or vessels, direct/indirect tank filling point, vapour recovery system, vent line and vent point, tank backfill sands or gravels, electrical cabling, corrosion prevention systems and interstitial monitoring systems (31).

New Zealand is one of the countries which is involved in marine oil activities as it is stated in the survey done for the year 1997. Those activities includes

- shipments of crude and condensate to Marsden point refinery (domestic imported)

- Tanker deliveries of finished products to New Zealand ports
- Cargo transfer operations involving crude oil or finished products
- Bunkering operations throughout New Zealand handling nearly 700,000 tonnes of bunker fuels (32).

Oil spills can occur during those activities which might lead to the environmental contamination of hydrocarbon fuel. Potential sources of oil spills as categorised by Lenting *et al* (32) include:

Coastal regions: Vessel incidents; collisions with another vessel, Grounding, Fire/explosion or structural failure, Foundering, ship to ship transfers, illegal discharges, and offshore oil production (at Taranaki only).

Ports: Vessel incidents; Collision with another vessel, Grounding, Fire/explosion or structural failure, Impact with wharves.

Transfer incidents; Overfilling tanks, Hose/line failure, Poor housekeeping, Wharf pipeline leaks, Storage terminal releases.

Other sources of fuel contamination might be due to urban runoff (10) which consists of a mixture of organic and inorganic materials, mineral particles, soot and other solid wastes, that are transported to rivers or coastal water sediments, especially during storm events.

Marine accidents are one of the sources of fuel spills in our environment. They occur suddenly and the negative effects are very evident. Some examples of the major accidents include: (33) Torrey Canyon 1967 which spilled 123,000 tonnes, Amco Cadiz 1976 which spilled 230,000 tonnes, The *Exxon Valdez* 1989 (31) which caused an oil spill of about 11 million gallons (38,000 tonnes) of crude oil, Brayer 1993 which spilled 84,000 tonnes and the Wales 1996 (33) which spilled 72,000 oil tonnes. In the case of Exxon Valdez, US\$ 3.5 billion has been used so far (2004) for cleaning up and

although the majority of the spill damaged area now appears to have recovered, pockets of crude oil remain in some locations, and there is evidence that some damage is continuing (34).

Apart from marine activities and large commercial tanks, in some countries there are many small underground tanks which are privately owned and have potential to cause significant environmental contamination (35). It is also reported by Michigan State University (35) that, there are many tanks in Michigan installed over years by farmers and home owners who did not record the location or contents of the tank. If this is the case, the possibility of having contamination from those tanks is much higher because the leak in an under-ground tank may not be discovered until groundwater is contaminated.

Furthermore, frequent small fuel spills when refuelling farm equipment may be reason for concern, just a small amount of fuel can pollute a well and the drinking water of many people, though the smell and taste of the water may appear normal. A petroleum spill can move rapidly into the soil and quickly contaminate drinking water. Petroleum storage problems can also affect the sale of a farm (35). In reality anywhere where fuels are handled and used is likely to have some degree of contamination.

In the study of soil water holding properties (36) it is also observed that the contamination of petroleum hydrocarbons to unsaturated soil affects the unsaturated hydraulic properties. It was observed that, at higher suction values, the water-holding capacity of soil contaminated by petroleum hydrocarbons increases because the introduction of a relatively low amount of oil contamination inhibits the movement of water which thereafter changes the soil's hydraulic properties (36).

There are hundreds of hydrocarbons found in petroleum. These exhibit widely differing toxicity and mobility characteristics and consequently differing human and ecological risks. Aliphatic hydrocarbons are generally less toxic to the environment as well as human health than the aromatic hydrocarbons of the same carbon number. The idea of using long chain hydrocarbon above C_{15} in this research is mainly because the smaller hydrocarbons have often evaporated from older spills and from a practical point of

view, the longer the chain the lesser the evaporation during soil sample preparation. It would be hard to mill short chain hydrocarbons such as hexane since it would evaporate.

On the other hand, it is important to note that there are some other chemicals that occur naturally at some level in all environments. These naturally occurring chemicals are inorganic or organic that is attributable to natural geological or hydrological characteristics of the particular area. Stout *et al* (2003) (10) refers these natural occurring hydrocarbons as “background hydrocarbons”, which have not been altered by human activities such as natural oil seeps, metals, or plant derived organic matter soils, forest debris, etc. However it is considered that the land is contaminated when the level of hazardous substance is greater than that which would naturally occur at the same site. Hazardous substances potentially pose an immediate or long-term risk to the health of humans or the environment. As stated above, they can be wastes from manufacturing processes, fuel storage, and residue from the past land uses such as agricultural activities.

1.3 A REVIEW OF SOIL REMEDIATION TECHNOLOGIES

There are number of destruction technologies used for chemical contaminants which depend on the variety of sources including contaminated soils, sediments, chemical stockpiles, building materials and waste dumps. These technologies include biological, thermal and chemical processes. The following is a summary of each process:

1.3.1 Biological Processes

Biological processes involve the use of naturally occurring enzymes in plants and microorganisms to catalyse the detoxification reactions. This technology is very cost effective mostly because a properly chosen organism will breed and flourish in the soil.

Biological processes can be divided into two groups, bioremediation, the process by which a living organism acts to degrade or transform hazardous organic contaminant;

and phytoremediation, which specifically uses plants to remediate soil or ground water. Although bioremediation holds great promise for dealing with intractable environmental problems with minimal site disturbance, when compared with conventional clean up technologies, more research is needed to determine how microorganisms interact with different environments (37).

An example of this is organochlorine pesticides. These are intended to kill living things, and most microorganisms cannot survive in high concentrations of the pesticides. This limits the use of biological processes in the destruction of pure pesticide disposal and remediation. Although biological treatment of contaminated soil is a well-established technology, a disadvantage of the technique is that the rates of degradation of hydrophobic compounds can be slow because of their limited bioavailability. Strategies to increase the bioavailability of compounds promoting biodegradation include the use of (bio) surfactants, oxidative enzymes, various chemical pretreatment methods, and partitioning into organic solvents (13).

Examples of Bioremediation of Soil Contaminants

Biodegradability of a compound is influenced by its physical characteristics, such as solubility in water, vapour pressure, and by its chemical properties, molecular structure and presence of various kinds of functional groups for initiation of biodegradation (1).

In biodegradation there are aerobic treatments and anaerobic treatments. Aerobic waste treatment utilizes aerobic bacteria and fungi that require molecular oxygen. These processes are often favoured by microorganisms, in part because of the high yield obtained when molecular oxygen reacts with organic matter. Aerobic waste treatment can be applied to hazardous wastes such as chemical process waste and landfill leachates (1).

In anaerobic waste treatment, microorganisms that degrade wastes in the absence of oxygen can be used on a variety of organic hazardous wastes. It requires less energy,

yields less sludge by-product, generates hydrogen sulphide which precipitates toxic heavy metal ions; and produces methane gas which can be used as an energy source (1).

The study conducted by Nam *et al* (38) showed that, bioremediation has limited applicability when soils are contaminated with complex mixtures of highly hydrophobic aromatic compounds such as soil from manufactured gas plant which occurs with tar residue. Therefore there was a need of combining chemical processing bioremediation.

The widely used reaction used for the destruction of organic contaminants including (poly)chlorinated aromatic compounds is Fenton's reaction which uses hydrogen peroxide catalyzed by ferrous ions to generate a strong non-specific oxidant hydroxyl radical that reacts with most organic compounds (refer to section 1.3.3) in aqueous solution or soils. Where this is to be followed by bioremediation, it needed to be modified. Nam *et al* (38) had to modify the Fenton reaction to a pH between pH 6-6.5 in order to enhance the degradation of PAH's since the low pH requirement of the reagent (pH 2-3) was incompatible with biological treatment.

One solution to the problems of hydrophobic compounds was found by Bardi *et al* (2000) (39). The use of β -cyclodextrin enhanced the degradation of both aliphatic and aromatic hydrocarbons by increasing their bioavailability. Cyclodextrins are natural compounds that form soluble complexes with hydrophobic molecules. The β -cyclodextrin was significantly effective at 1% concentration and enhanced the degradative activity of a natural microbial soil population on both aliphatic and aromatic hydrocarbons (39).

These examples explain how difficult it is to have favourable conditions for microbial growth as well as conditions required for the destruction of toxic compounds. For the most successful and rapid bioremediation, the oxygen, pH and nutrient concentrations, as well as temperature must be carefully controlled. The cost of extra reagent can add significantly to the total cost of remediation.

Examples of Phytoremediation of Soil Contaminants

Phytoremediation is a specific form of bioremediation that uses green plants to remove, contain, or render harmless environmental contaminants. It is a promising technology that addresses clean-up of organic solvents, PCB's, heavy metals, polyaromatic hydrocarbons, explosives and energetics, or nutrients.

In the early '90s, phytoremediation of environmental contamination emerged with promises of significant economies reminiscent of those initially proposed for bioremediation. It was proposed that toxic organic compounds might be degraded by the action of microorganisms peculiar to the rhizosphere of plants. The plant rhizosphere is defined as being within the rooting zone plants and includes the root, soil attached to the roots, and adjacent soil that is influenced by the root (40).

The potential economic benefits of using plants for remediation are impressive. Plants are robust and “solar powered”. Their root systems permeate soil and sediment environments with an extensive and active membrane system. The soil near their roots has microbial populations orders of magnitude greater than non-root soil. These benefits are provided with little or no maintenance requirements. Furthermore, plant-based systems are welcomed by the public due to their superior aesthetics and the societal and environmental benefits that their presence provides (41).

Unfortunately, experiments with enhanced rhizosphere microbial degradation of toxic organics such as polyaromatic hydrocarbons have yielded only small increases in degradation rate and marginal improvements in the ultimate residual pollution levels that can be achieved. Studies of the use of deep-rooted trees have shown that chlorinated hydrocarbons (CHCs), such as the most common groundwater pollutant, trichloroethylene (TCE), are taken up by trees and are also degraded in tree plantations; but degradation rates are low and large areas are required for such plantations.

At present, it seems that phytoremediation is largely a niche technology and cannot play a major role in providing the order-of-magnitude cut in remediation costs that is urgently needed (41).

Water hyacinth is just beginning to be used for phytoremediation. Water hyacinth (*Eichhornia crassipes*) is a fast growing, free-floating aquatic weed. This use came about for a few reasons, the first being that water hyacinth is so plentiful. People have been trying to remove the plant from many water ways, spending billions of dollars in doing so. In many cases this removal is almost impossible. It has been discovered that water hyacinth's quest for nutrients can be turned in a more useful direction (42).

The water hyacinth has been shown to remove eutrophying nitrogen and phosphates, as well as heavy metals. Most of the common heavy metals that are in water are positive ions. One possible mechanism of remove them would be to put a negatively charged object into the water and use it to attract the positively charged ions. This is essentially what happened when the roots of a water hyacinth plant are put into the polluted water. The roots of many plants, including water hyacinth, have a negative charge to them. When put this negative charge into the water it attracts positively charged ions (42).

Studies were conducted for the heavy metal removal by water hyacinths (43), and the uptake of arsenic, chromium, mercury, nickel, lead and zinc from the aqueous solution for six different concentrations ranging from 5 mg/L to 50 mg/L was investigated. Results indicated that at lower concentrations i.e. 5 mg/L of heavy metals, the plant growth was normal and removal efficiency was greater. At higher concentrations, greater than 10 mg/L, the plant started wilting and removal efficiency was reduced.

It was observed that in aqueous solutions containing 5 mg/L of arsenic, chromium and mercury the maximum uptake was 26 mg/kg, 108 mg/kg and 327 mg/kg of dry weight of water hyacinth respectively. Finally, it was concluded that by using water hyacinth, heavy metals could be effectively removed from wastewater when their concentrations were less than 10 mg/L. Lead and zinc were removed more efficiently at higher concentrations than other metals, but plants started to discolour at high concentrations of metals and this high uptake leads to destruction of plants in most cases (43).

This treatment system has advantages of the low costs of operation compared to other conventional mechanical treatment systems when applied to small and medium sites. Also, it has been shown (44) that the system can operate with a high efficiency to remove nitrogen, phosphorus and heavy metals. When the wastewater is free of toxic compounds, the nutrients are recovered and transformed in valuable biomass. On the other hand, the main limitation for the application of this kind of non-conventional system is that it requires larger areas of land, although it can use marginal land. Also, if mismanaged, mosquitos and noxious odours may disturb the surroundings. Plants must be disposed of safely when hazardous compounds are removed from the wastewater (44).

1.3.2 Thermal Processes

Thermal processes involve the use of high temperatures to provide the energy necessary for oxidation, reduction and rearrangement reactions to take place. The temperature involved is over 1000°C and the reactions are fast. Destruction efficiencies are usually near 100% however it requires extensive gas cleaning to achieve it. High temperature incineration is a collective term applied to a range of proven incineration technologies, which achieve high destruction efficiencies.

As an example of some of the issues associated with incineration internationally, high temperature incineration is the most widely employed means to destroy chemicals, but in recent years; public opposition to it has increased due to uncertainties over its potential for undesirable side products such as dioxin emissions (45) from the destruction of chlorinated organics. Dioxin is known to be associated with cancer development in humans. In Japan, where municipal waste contains relatively high levels of the chlorine containing plastics such as PVC, high dioxin concentrations in soils surrounding a municipal waste incinerator were found to be well correlated with high cancer rates among the surrounding populations (46). Also it is reported that in Spain over a period of two years, dioxin in the blood lipids of people living near an incinerator burning urban wastes increased by 10-15 percent, in addition their blood lipid levels of PCB's increased about 5 percent (46).

Dioxin refers to a class of structurally and chemically related halogenated aromatic hydrocarbons that includes polychlorinated dibenzodioxin, polychlorinated dibenzofurans and the “dioxin-like” polychlorinated biphenyls. The route from the dioxin exposure in the environment to body burden is predominantly through food. It has been reported currently that the main source of human exposure, around 95% is from diet, particularly dairy products, meat and oil fish (47). However, previous studies indicated that the level of dioxin in the general population of New Zealanders is in the low to medium range relative to more industrialised countries (24).

It has been concluded that in order to form dioxin the process must include:

- (a) Incomplete combustion of organic material. Carbon present in the ash provides a ready platform for dioxin formation and higher levels of residual organic matter and lesser burnt-out materials are associated with higher level of dioxin
- (b) Trace metals for catalysis. Copper is an important component of the fly ash and in the presence of chloride is an excellent catalyst for the formation of dioxins by serving as an effective chlorine donor
- (c) Temperatures between 250 and 450°C, with the peak production temperature being around 325°C. Dioxins are a product of elevated temperatures but they are destroyed above 800°C.
- (d) A chlorine source. The toxic dioxins contain chlorine in at least four positions and generally come from organo-chlorine compounds. Inorganic chlorine such as sodium chloride, are very poor sources of chlorine (47).

High temperature incinerations of possible interest to New Zealand include rotary cement kilns, plasma, fluidised bed combustion and controlled air incineration (pyrolysis). In New Zealand any proposal to use high temperature incineration for the disposal of hazardous waste could be expected to focus public interest and concern on the possibly of dioxin formation and emission from such a facility (45).

Cement kilns

Cement kilns are inclined rotating cylinders lined with refractory brick that are internally fired. They are designed and constructed to heat materials, such as limestone, clay and sand. The raw feed materials are fed into the higher, elevated end of the kiln. As the kiln slowly rotates, the raw meal tumbles down toward the hot lower end and is gradually altered physically and chemically at temperatures as high as 1500°C. Combustion gases enter the kiln at the hot lower end and flow upward, heating the raw materials flowing in the opposite direction as they pass over and exit the kiln at the top end. The gases then pass through air pollution control devices before entering the atmosphere (46).

The advantage of cement kilns is that large amounts of waste can be processed at a time or on continuous basis. However, not all cement kilns are suitable for incineration of certain group of hazardous waste. Special equipment is required to inject the hazardous waste such as pesticides into the kiln. Such equipment is expensive and requires expert supervision (46). Cement kilns also poses threat to the workers, surrounding populations and the environment due to the emission of the cement kiln dust which is also known to contain dioxins (46).

Plasma arc

Plasma arc treatment involves directing an electric current through a low-pressure gas stream to create a thermal plasma field. Plasma arc fields can range from 5,000°C to 15,000°C. The high temperature dissociates waste into its atomic elements. By injecting the waste into plasma, or by using plasma arc as a heat source for combustion or pyrolysis, this technique can effectively treat not only most types of non-aqueous inorganic sludges containing heavy metals but also solid or liquid organic and highly halogenated materials such as fire retardants and ozone layer depleting chloro-fluorocarbons (46). The waste stream from the plasma arc destruction have been described as essentially the same as those from incineration, such as combustion by-products and salts (48).

Various plasma reactors have been developed for the thermal destruction of hazardous waste, this includes, Plasma Arc Centrifugal Treatment (PACT), In Flight Plasma Arc system (PLASCON) and Plasma electric waste converter (STARTECH) (46).

1.3.3 Chemical Processes

Chemical processes involve the use of strong chemical oxidants or reductants to destroy hazardous chemicals. Additional energy in the form of heat, electricity, mechanical activation and radiation is necessary to increase reaction rates, since reactions with chlorinated aromatics are not fast even if the strongest oxidants and reductants are used (49). On the other hand, advanced oxidation processes may be necessary when time constraints or other logistics require consideration.

Example of chemical process is *in situ* chemical oxidation, which is based on the delivery of chemical oxidants to the contaminated media in order to destroy the contaminants by converting them to innocuous compounds commonly found in nature (50). The most common field applications use the Fenton reagent (50), which involves catalysed decomposition of hydrogen peroxide (H_2O_2) by iron (II) to form hydroxyl radicals (OH^\bullet).



It has been applied to the treatment of surface soils, subsurface soil and underground water (49).

Hydroxyl radicals are electrophiles and strong oxidants that react with most organic substances. The most common mechanism for hydroxyl radicals is electrophilic addition to alkenes or aromatic rings, while hydrogen abstraction often occurs with saturated compounds (17).

However, several modifications have been developed for specific environmental applications, including catalysis by iron chelates to promote reactions at near neutral pH, catalysis by iron oxyhydroxides in soil and high H_2O_2 concentrations to promote contaminant desorption from soils (49).

Fenton's reagent is produced *in situ* by adding an iron catalyst to a hydrogen peroxide solution. It can be applied to a variety of soil types and sizes such as silt and clay. It is used to treat volatile organic chemicals including dichloroethene, trichloroethene, tetrachloroethene and benzene, as well as semi-volatile organic chemicals including pesticides, PAH's and PCB's. The most common oxidant delivery method involves the injection of the reagent to the contaminant zones which require both injection and extraction wells (51), Figure 1.2. The number and pattern of injection and extraction wells and monitoring wells must be designed to ensure maximum coverage of the treatment zone (51).

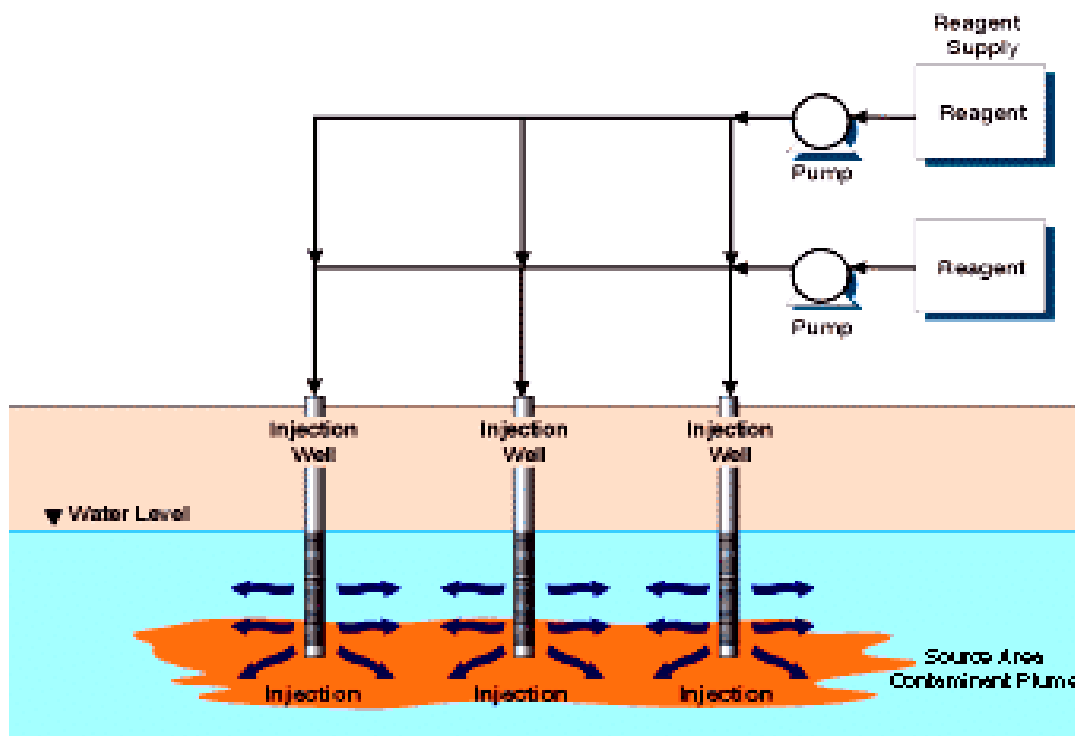


Figure 1.2: Chemical oxidation – In situ Remediation Technology

Source: http://enviro.nfesc.navy.mil/erb/restoration/technologies/remed/phys_chem/phc-43.asp

However, the subsurface heterogeneity can cause uneven distribution of oxidants and there is no control of the subsequent movement of the oxidant after its release. Also, naturally occurring buffering agents, such as carbonates, may prevent the pH from being reduced to the required level (between 3 and 6). In addition, Fenton's reagent is toxic to microbial populations (52). Further, use of this technology may reduce porosity of the subsurface due to the formation of metal oxide precipitates.

1.4 BALL MILLING

Mechanochemistry (tribochemistry) is a term referred to chemistry occurring at surfaces under impact (27). Chemical reactions required energy; a ball mill can be used as the source of mechanical energy during reactions. High energy impact between surfaces of balls and container walls can produce transient temperature rises of large magnitude. Such agitation can produce marked chemical activation, resulting in reactions between the mill charge components and reactions with the mill surfaces (28).

At this stage the principal interest of most researchers is in the destruction of mostly chlorinated organic pesticides. However the results of this study show it has considerable potential for other molecules and there is also some evidence that ball milling has potential as a solvent free chemical reaction process (27).

The ball mills used are derived from orbital ball mills used in the mining and chemical industries. The design is a steel drum containing hardened steel balls. Waste and reactants are loaded into the mill and cyclically rotated for a sufficient length of time. However, there are different designs of ball mills; they differ in their capacity and efficiency of milling. A brief description of different types of ball is provided below.

1.4.1 Planetary ball mill

The planetary ball mill e.g. Fritsch Pulverisette mills (Figure 1.3) owes its name to the planetary orbit- like movement of its vials. These are arranged on a rotating support disk

and a special drive mechanism causes them to revolve on their own axes. The centrifugal force produced by the rotating support disk both act on the vial contents, consisting of material to be ground and the grinding balls. As the vial and the supporting disk rotate in opposite directions, the balls inside have a centripetal acceleration. This causes the grinding balls to run down the inside wall of the vial; the friction effect, followed by the material being ground and the grinding balls lifting off and travelling freely through the inner chamber of the vial and colliding against the opposing inside wall; the impact effect. Grinding balls and vial are available in different materials such as agate, silicon nitride, chrome steel, plastic etc. (53).

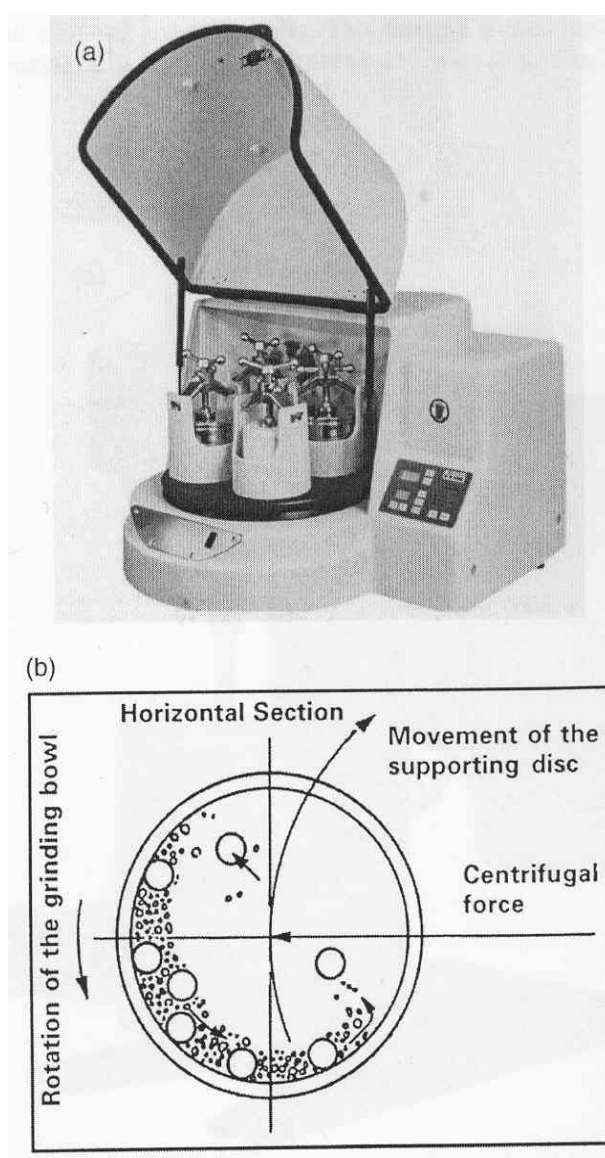


Figure 1.3: a) Fritsch Pulverisette P-5 four station ball mill. (b) Schematic depicting the ball motion inside the ball mill.

1.4.2 Attritor mills

A conventional ball mill consists of a rotating horizontal drum half filled with small steel balls (Figure 1.4). As the drum rotates the balls drop on the material that is being ground. The rate of grinding increases with the speed of rotation. At higher speed the centrifugal forces acting on the steel balls exceeds the gravitational force, and the balls are pinned to the wall of the drum; at this point the grinding action stops. A attritor consists of vertical drum with a series of impellers to energize the ball charge, causing size reduction of the material being ground because of the impact between balls, between balls and container wall, and between balls, agitator shaft, and impellers. Attritors are mills in which large quantities of material to be ground. From 0.5 to 40 kg can be milled at a time (53).

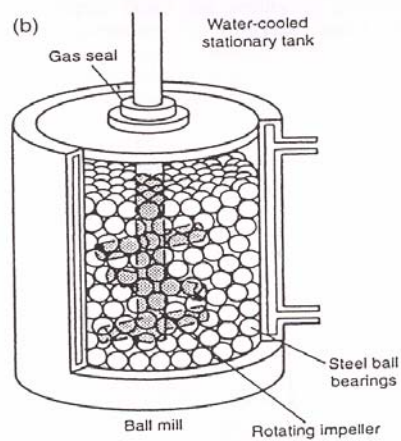
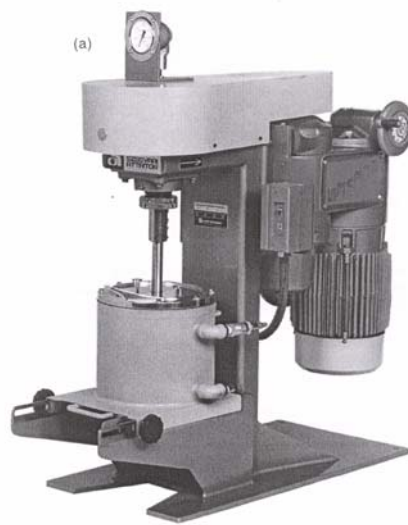


Figure 1.4: a) Model 1-S attritor. (b) Arrangement of rotating arms on a shaft in the attrition ball mill.

1.4.3 SPEX shaker mills

The common variety of SPEX shaker mill has one vial, containing the sample and grinding balls, secured in the clamp and swung energetically back and forth several

thousand times in a minute (Figure 1.5). The back and forth shaking motion is combined with lateral movements of the ends of the vial. With each swing of the vial the balls impact against the sample and the end of the vial, resulting in both the milling and mixing of the sample. A variety of vial materials are available including, stainless steel, alumina, plastic, silicon nitride etc (53).

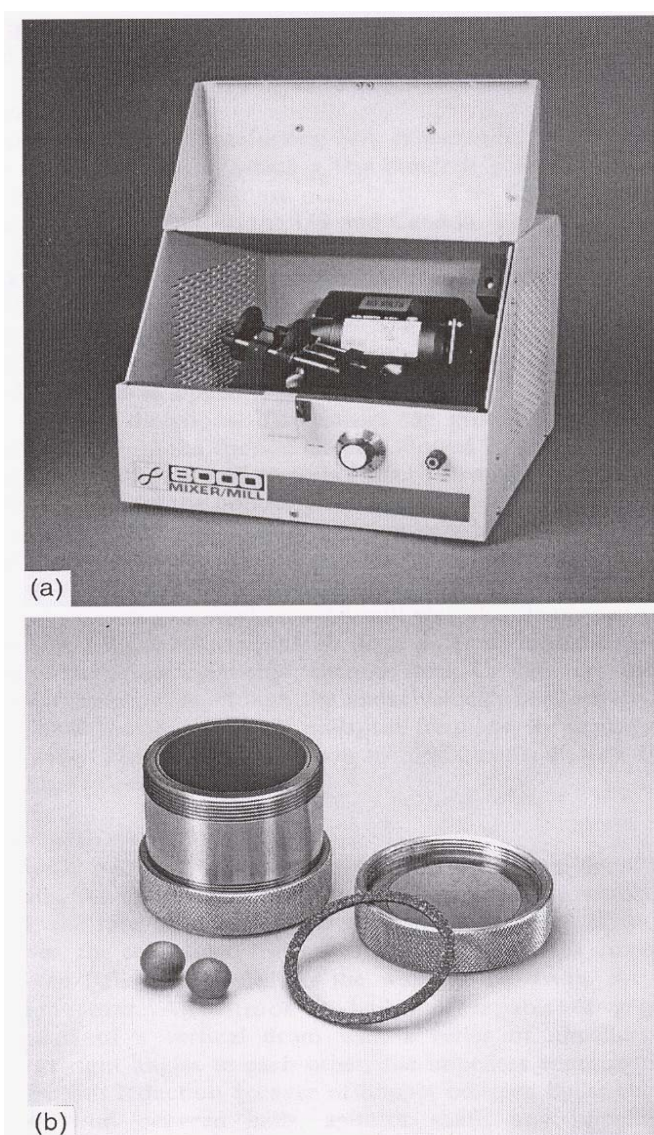


Figure 1.5: a) SPEX 8000 mixer/mill in the assembled condition. (b) Tungsten carbide vial set consisting of the vial, lid, gasket, and balls.

1.4.4 Retsch S100 Centrifugal

As stated earlier, a Retsch S100 Centrifugal Ball Mill (Figure 1.6) was used in this study. “The Retsch S100 centrifugal ball mill is designed for fast loss-free grinding and mixing of many types of soft/medium, hard/brittle materials, either dry or in suspension. Maximum feed size < 10 mm; final product < 1 micron. Simple to operate, the mill features ergonomic touch-sensitive control panel, timer, speed regulation and hinged plexiglass cover. Processing takes place within grinding jars which are available in various sizes and a choice of materials to avoid contamination due to abrasion from the grinding process (54). The speed is adjustable from 0 to 550 rpm. The centrifugal forces which are generated propel the grinding balls against the inside wall of the jar where they roll over the material to be ground. Grinding is effected primarily by impact and fraction. To counter any agglomeration effects and to enhance the homogenisation quality, the mill is fitted with an automatic reverse action system. The 100-watt brake motor brings the unit to a complete stop in less than one second after the prescribed time elapses, or after the safety cover has been opened (54)”.

(a)

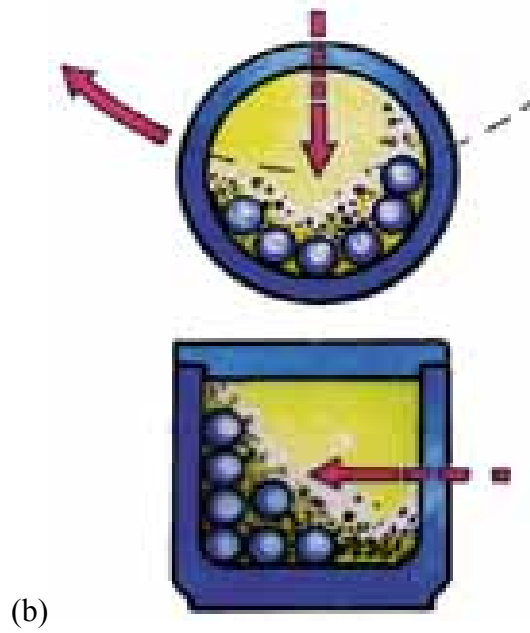
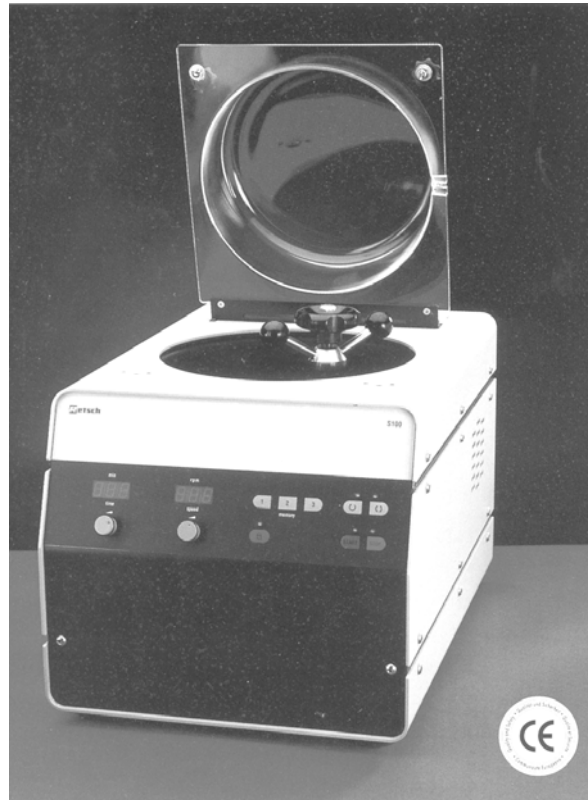


Figure 1.6: a) Retsch S100 Centrifugal Ball Mill. (b) Schematic depicting the ball motion inside the ball mill.

The ball milling process is a mechanochemical process, relying on the energy released at the point of collision between balls in a ball mill to activate reaction between the waste and the reactant, breaking down organic compounds (55). The process may be applied to concentrated forms of halogenated hydrocarbons and it is likely to readily treat wastes containing a range of organic contaminants.

Ball mills reduce the potential for the release of contaminants because of the low energy potential of the system. The process operates at low temperatures, increasing safety, and with relatively low energy consumption and, in the case of chlorinated aromatic compounds, reducing the potential for the formation of dioxins. The process largely uses well-established mineral processing equipment and principles and no gaseous emissions are produced. During the process, there is high degree of mixing of wastes as well as break up of agglomerated material. Finally, the process can be readily shutdown in a short period of time (55).

1.5 KINETICS OF COLLISIONS AND MILLING KINEMATICS

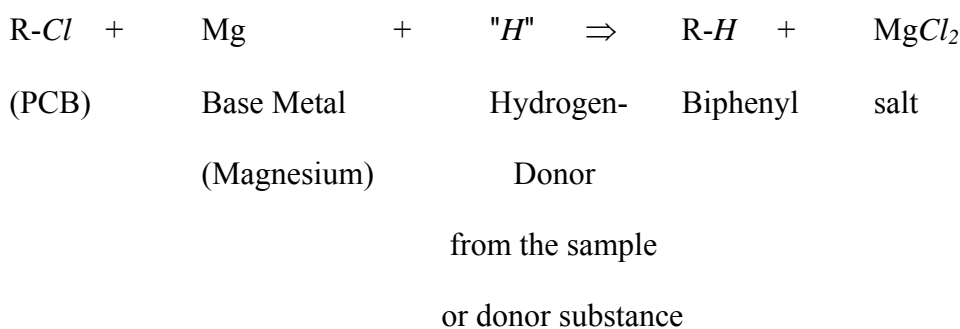
During milling, the forces inside the mill are generated due to the impacts encountered. For example in the case of contaminated soil, there are impacts between ball-ball, ball-wall and ball-corner, ball-soil, soil-soil, and soil-wall. During milling it is noted that the mill filling of the power shaft have an effect in the power draw. A decrease in the filling level leads to a decrease in the power consumption; this is because all the material in the mill contributes to power consumption to one degree or another. The power draw is also varied with the function of time for different mill speed, since power is the product of the torque and the angular speed of the mill. A higher mill speed results in a greater power draw if all other conditions remain the same (56, 57). However for any particular combination of ball type, number of balls and charge load, there is an optimum speed for maximum power and above that power starts to drop (58). After allowing for frictional losses it is assumed that the power used is proportional to the power put into the material being ground.

1.5.1 Physical and Chemical Effect results from mechanochemical treatment (ball mill)

- In milling there is modification of new physicochemical properties by changes in (i) Surface activity including tribochemical activation, surface activity is changed due to the particle reduction of the milling component, the smaller the particle sizes obtained, the higher the surface area for the reaction. (ii) Vapour pressure where by larger particles have lower vapour pressure and smaller particle have higher vapour pressure (29).
- Acceleration of chemical reactions of both homo and heterogeneous kind such as (i) Catalytic activity (ii) Cold solid state reactions (iii) tribochemical decompositions of organic molecules.
- Favouring of surface reactions which may be caused by bond breakage such as (i) Formation of free radicals which may initiate a chain reaction (ii) Catalytically influencing the oxidation and reduction rate (iii) Hydration and corrosion
(iv) Generation of electric charges (v) Breakdown of starting materials and further decomposition of intermediates (29).

1.6 PREVIOUS RESEARCH CONDUCTED USING BALL MILLING AS A DESTRUCTING DEVICE

As noted in the introduction, previous studies conducted using a ball mill involve addition of other chemicals to facilitate the rate of chemical reactions. Birke V. (59) developed a method known as dehalogenation by mechanochemical reaction (DMCR) which utilises alkali or alkali earth metals such as magnesium or sodium as dehalogenation reagents in the mechanochemical reaction of ball mill and stated that the method is very quick and efficient in eliminating toxic substances in polyhalogenated pollutants. The equation can be presented as follows:



TOXIC \Rightarrow much less harmful

From the above equation the hydrogen donor in the ball milling reaction can be obtained from the sample itself or can be obtained by addition of some hydrogen donating substances such as alcohols and polyethers.

Previous researchers also used additional chemicals such as sodium and base metals like magnesium to facilitate the rate of reaction (59). More exotic materials such as the hydrides $NaBH_4$ or $LiAlH_4$ have been used. Aresta M *et al* (2002) (60) used solid hydrides $NaBH_4$ or $LiAlH_4$ at different ratios of hydride/soil (5%, 3%, and 2.5%) and milled for different length of time (3.5-3.0 Hrs). The products obtained at the end of the reaction were biphenyl and chloride salts and no hazardous byproducts were detected. The disadvantage of using hydrides is that they are difficult to handle and have relatively high costs.

In the study conducted by Field D. L *et al* (1997) (27) where alumina and silica were used in the ball milling at ambient temperature for 24 hrs all the hydrocarbons were converted largely to carbon (graphite). However, there were some other products obtained at intermediate stages such as tetralin, phenylcyclohexane, bicyclohexyl, 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene, 1,2,3,4,4a,9,9a,10-octahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene, 1,2,3,4,4a,9,9a,10-octahydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene. The results of this research was interesting since it showed that aromatic hydrocarbons treated mechanically with apparently non reactive matrices (alumina and silica) were also destroyed. This is one of the few

examples that clearly show there is a potential to study chemical transformation and not just the destruction.

Mechanochemistry of naphthalene as observed by Field D. L. (1997) (27) showed that the presence of carefully dried alumina will cause naphthalene to deuterate to 74% at the α position and 74% at the β position, this leads to the formation of tetralin as shown in the figure below, with deuterium content indicated in structure (1), Figure 1.7. The residual naphthalene has deuterium content indicated in structure (2), Figure 1.7.

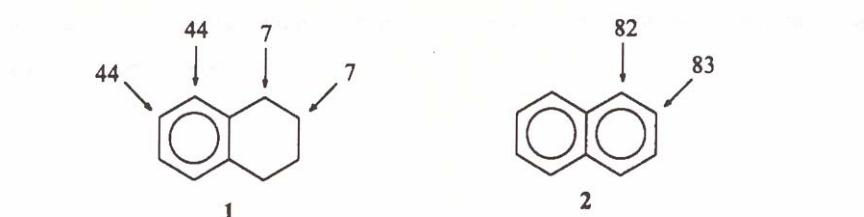


Figure 1.7: Percentage deuteriation at different positions in dry alumina.

However, they showed that, by using alumina wetted with D_2O , deuterated naphthalene (structure 3, Figure 1.8) and deuterated residual naphthalene (structure 4, Figure 1.8) were formed. It was also shown that the mechanohydrogenation reactions of naphthalene and biphenyl are highly sensitive to the nature of alumina used as the catalyst. This has some implications for other work. The nature of the substrate may have a significant influence on the results.

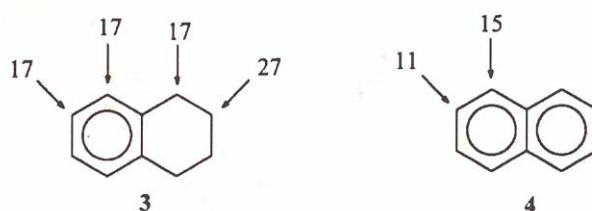


Figure 1.8: Percentage deuteriation at different positions in alumina wet with D_2O .

In further studies (61) on the destruction of naphthalene using alumina as the inorganic matrix, they reported that the treatment of a number of hydrocarbons in a vibratory mill with approximately ten-fold weight of silica or alumina under nitrogen, air or oxygen will result in a complete conversion to graphite, though at an intermediate stage significant quantities of partially reduced products e.g. tetralin from naphthalene and phenylcyclohexane from biphenyl were also formed.

In this study they proposed three classes of mechanism for the reactions resulting in partially reduced products:

- (i). The partially reduced compounds could arise *via* a stepwise transfer of hydrogen atoms.
- (ii). Alternatively, they could arise from electrocyclic transfer of pairs of hydrogens, given that under mechanochemical conditions it may be possible for a molecule to undergo quite unusual processes.
- (iii). Finally, stoichiometry requires the production of molecular hydrogen to account for all the original carbon being converted to elemental carbon. Therefore the partially reduced intermediates, such as tetralin from naphthalene, could result from “mechanocatalytic” hydrogenation. This mechanism is not attractive because alumina is not a likely candidate for a hydrogenation catalyst, but at least there was an indication that the reduction was matrix specific (it does not occur with silica).

Considering the above suggestion knowledge concerning formation of radicals in the Naphthalene reaction seems to be important.

1.7 NAPHTHALENE RADICALS

Perkins (1994) (62) defined radicals as a molecular entity containing one or more unpaired electrons. However he stated that transition metal ions, or atoms of the alkali metals would seldom be referred to as radicals, although at the other end of the periodic table, halogen atoms are more commonly included. The definition also includes species

formed from familiar organic molecules by the loss or gain of a single electron for example the naphthalene radical anion (Figure 1.9).

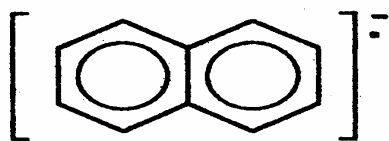


Figure 1.9: The naphthalene radical

According to W.J. van der Hart (63) in naphthalene radical cations there are two essentially different types of hydrogen shifts. Figure 1.10, gives an overview of all structures that can be formed from the naphthalene radical cation by 1,2-hydrogen shifts where the horizontal arrows describe shifts of an sp^2 bonded hydrogen and the diagonal arrows of an sp^3 bonded hydrogen (63).

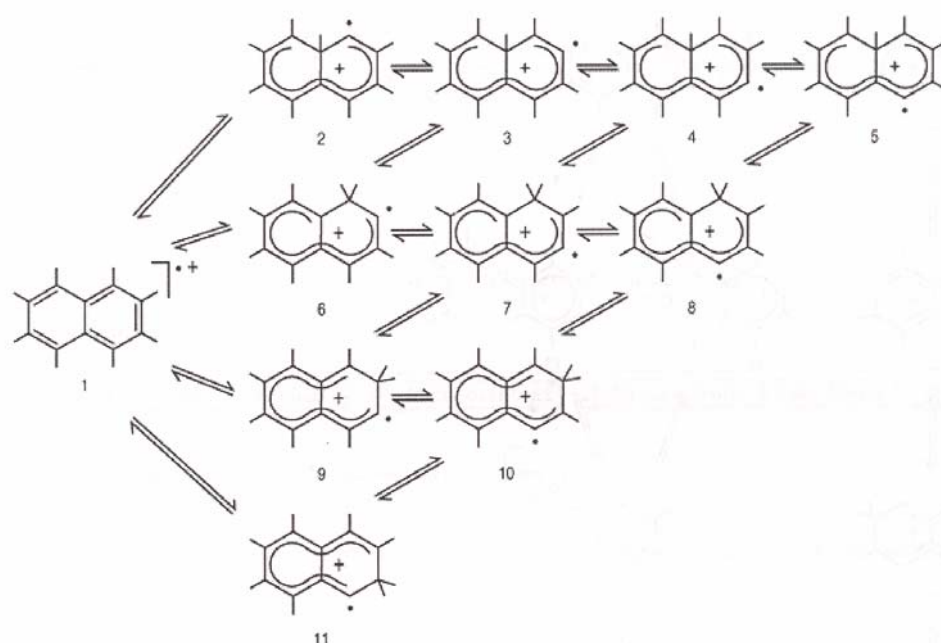


Figure 1.10: Reaction scheme for hydrogen shifts in the naphthalene radical cation

Similar mechanisms will occur for anthracene and phenanthrene.

1.8 ALIPHATIC HYDROCARBON DEGRADATION

The fragmentation pattern in the mass spectrum is characterised by clusters of peaks, and the corresponding peaks of each cluster are 14 (CH_2) mass units apart. The largest peak in each cluster represents a $\text{C}_n\text{H}_{2n+1}$ fragment; this is accompanied by C_nH_{2n} and $\text{C}_n\text{H}_{2n-1}$ fragments. The most abundant fragments are C_3 and C_4 , and the fragment abundances decrease in a smooth curve down to $\text{M}-\text{C}_2\text{H}_5$; the $\text{M}-\text{CH}_3$ peak is characteristically very weak or missing. Compounds containing more than 8 carbon atoms show fairly similar spectra (63a). It is assumed that the long chain hydrocarbon will fragment a similar way during ball milling.

This was also found in the aliphatic hydrocarbons analysis that there were no fragmentations observed in the GC, presumable because the short chain fragments which might have been formed during the milling will have been lost.

1.9 AIM OF THE RESEARCH

When contamination is at a level that it poses a risk to the environment and to humans, steps must be taken to remediate the soil.

As discussed in the introduction section there are different methods for the destruction of organic contaminants. In this research mechanochemical reaction for the destruction of chemicals was investigated using a laboratory scale ball mill as the source of the mechanical energy. So far ball milling has been used for the destruction of organochlorine pesticides like DDT, PCB, and Pentachlorophenol. This research will be based on the destruction of PAH's and long chain aliphatic hydrocarbons as representative of two significant environmental problems.

Ball milling involves relatively low technology, and is easy to operate. It does not involve high temperatures, does not need expensive chemicals and can be made portable.

As discussed earlier, naphthalene, anthracene and phenanthrene were chosen as the example of PAH's and the hydrocarbons, n-eicosane (C20), n-tetracosane (C24) and n-octacosane (C28) were used as the models for long chain hydrocarbons.

The experimental plan was:

1. To use ball mill as a mechanical reactor to destroy PAH's in soil and observe if the destruction process is taking place.
2. To use ball mill as a mechanical reactor to destroy long chain hydrocarbons in soil
3. To provide data on the level of destruction encountered by mechanochemical process.

4. To use different types of soil: scoria soil, clay, silica sand, organic rich soil and slag to observe effect of soil type in destruction processes. This is because different soil properties may have an effect in the pesticides contamination and mostly important in the destruction process.
5. To change milling conditions, milling time and ball ratio and observe if changes of milling conditions have an impact to the destruction process.

CHAPTER 2

2.0 MATERIALS AND METHODOLOGY

2.1 MATERIALS AND EQUIPMENT

All the experiments were conducted at the Applied Science laboratories, Faculty of Science and Engineering, Auckland University of Technology, Wellesley campus, Auckland, New Zealand.

Milled scoria was collected from an undergraduate milling experiment, although the source is uncertain it is most probably from the Winstone quarry at Three Kings, Auckland and was considered typical of a local soil matrix. Clay was collected from excavations at 20 St. Paul Street, Auckland, and organic rich soil was collected from a private residence in Mt. Eden, Auckland. Silica sand (Mataia silica sand) was from Sand Resources (NZ) limited and slag (smelter slag) was from Slag reduction company (NZ) limited. Chemicals used includes; naphthalene (BDH-laboratory reagent), anthracene (Peking's reagent), phenanthrene (BDH-analytical grade), n-tridecane- (SIGMA 99%), n-eicosane (SIGMA 99%), n-tetracosane (SIGMA 99%), n-octacosane (SIGMA 99%), hexane (MERCK-HPLC grade), and acetone (ASCC 100%), Toluene (Fisher), Diethyl ether (BDH- analytical grade). Equipment used are: Sonicator (F.11i CAVALLIN, made in Italy), Centrifuge (MSE), Centrifugal Ball mill Retsch model S100 with jar of 500ml and balls of 20mm diameter, GC/FID (GC-17A, Shimadzu Corporation, made in Japan) and GC-MS (QP 5000), Shimadzu Corporation, with DB5 column 30M X 0.25 mm ID and DB-1.

2.2 METHOD

2.2.1 Preparation of Calibration Standards for PAHs and Aliphatic Hydrocarbons

Naphthalene standard solution of different concentration were made; 5000, 2000, 1000, 500 and 100 ppm. Each contained n-tridecane as internal standard. These standards were made to be used in the calculation of destruction rate of the contaminant in the soil after treatment. Standard solutions were stored in volumetric flasks tightly stoppered.

Anthracene and Phenanthrene standard solutions of different concentration were also made at concentrations of 2000, 1000, 500, 200 and 100 ppm. Each contained n-tridecane as internal standard. The solvent used for anthracene was toluene while for phenanthrene diethyl ether was used. These solvents were chosen based on minimal interference with the GC retention times and the solubility of the analytes.

For aliphatic hydrocarbons, n-eicosane and n-octacosane standard solutions of different concentration were made at the concentration of 10000, 5000, 2000, 1000, and 500 ppm in hexane. Each contained n-tetracosane as an internal standard. Again, care was taken to keep the solutions tightly stoppered.

2.3 SOIL SAMPLE PREPARATION

2.3.1 Soil contaminated with naphthalene

For each type of soil (scoria, clay and organic rich soil), 500 g of soil was spiked by a known amount of contaminant, 0.5 g of naphthalene in 100mL of hexane to give a final concentration in the soil of 1000 ppm naphthalene. The contaminated soil was left to dry in the fume hood overnight before starting milling. While there was a small loss due to volatilization, this was found to be only a few percent and exact concentrations were determined by the analysis.

Another batch of contaminated organic soil was made by using 0.5 g of naphthalene into 250 g organic soil to give 2000 ppm. This soil was used for experiment of naphthalene destruction with and without BHT.

As noted above losses due to volatilization particularly for naphthalene during drying period were originally a concern. Two different experiments were conducted to observe the volatility of naphthalene. The results showed that if the sample left for more than two days there was a significant loss of naphthalene. Therefore, after the sample was dried it was stored in a closed glass container and the milling was done not more than two days after sample preparation.

Volatilization check for naphthalene

Procedure 1:

100 g naphthalene contaminated soil (2500 ppm) with was placed in the mill jar with 20x20mm balls, milled at 300 rpm for 2 minutes to disperse the naphthalene, a sample was taken for analysis. The jar cover was left in place and the jar sat in an oven at 100°C for 30 minutes, the jar was removed from the oven and placed in the ball mill, milled at 300rpm for 2 minutes, sampling was done and the procedure was repeated to obtain three more samples. The samples were extracted and analysed in the usual way.

Procedure 2:

25 g of naphthalene contaminated soil (2000 ppm) was left in the fume hood without being covered for several hours, samples for analysis was taken after 2, 3, 5, 6, 36, 72hrs.

2.3.2 Soil contaminated with anthracene

For each type of soil (scoria, and silica sand), 200 g of soil was spiked by a known amount of contaminant, 0.5 g of anthracene in 100 mL of toluene to give final concentration in the soil of 2500 ppm anthracene. The contaminated soil was left to dry in the fume hood overnight before starting milling.

2.3.3 Soil contaminated with phenanthrene

For each type of soil (scoria, and silica sand), 200 g of soil was spiked by a known amount of contaminant, 0.5 g of phenanthrene in 100mL of diethyl ether to give final concentration in the soil of 2500 ppm phenanthrene. The contaminated soil was left to dry in the fume hood overnight before starting milling.

2.3.4 Soil contaminated with aliphatic hydrocarbons

200 g of soil was spiked with a known amount of contaminant, using 1g of n-eicosane and n-octacosane in 100mL of hexane to give a final concentration in the soil of 5000 ppm n-eicosane and n-octacosane. The contaminated soil was left to dry in the fume hood overnight before milling. This contaminated soil was used for the experiments of aliphatic hydrocarbons with and without addition of BHT or aluminium metal.

Another batch of soil contaminated with n-octacosane was made using scoria and slag. 5 g of n-octacosane was added to 200 g of scoria and slag separately to gave each the concentration of 25,000 ppm. This batch was used for the destruction of n-octacosane by milling 50 g sample.

2.4 MILLING PROCESS

For orbital mills, milling parameters such as ball ratios, milling time, milling speed, and ball to sample weight ratio may influence the end products of the milling process. It was found by Zhao (64) that, in order to have better milling results, longer milling times, a higher ball to sample ratio and larger milling balls were required (64). Milling time is of large significance for the properties of the milled powder and for the efficiency of the milling process.

It was found that breakage of particles is the major mechanism at long milling time. However, the milling time must be optimised with regard to both destruction rate and time to have economical production.

The variables such as milling speed, ball size and ball number interact in different ways. Ball size influences the milling process because small balls do not supply as much energy during collision for deformation and breaking compared to larger balls. The collision energy depends mainly on ball mass and ball velocity during the milling process. Since the velocities of the balls are dominated by the rotation rate of the rotor in the limited chamber space, the ball mass plays a more important role in determining the energy (64). However, higher numbers of balls with a smaller size will provide more collisions per unit time even though the energy of each collision is lower due to the reduced mass of each ball (65).

Milling speed affects the kinetic energy of the milling process. The kinetic energy of balls on the impact with the powder particles reduces as the rotation speed of the mill decreases (65).

In this study the milling process was done at a fixed speed (500rpm) using different ball ratios and different soil types in order to observe their effects on the destruction process.

2.4.1 Different ball ratio

100 g of naphthalene contaminated scoria (as from section 2.3.1) was used for ball milling in four different batches, batch with 20 balls, 10 balls, 5 balls and 1 ball. The milling was done at 500 rpm for 30, 45, 60, 120 and 150 minutes.

2.4.2 Different soil types

The milling procedures and sample preparation was the same as in section 2.4.1, but two different types of soil were used, scoria and clay soil.

2.4.3 Naphthalene destruction with and without BHT

Because the milling process is essentially dry, it is thought that free radical formation and propagation on surfaces is the principle destruction mechanism. The effect of adding the free radical scavenger, BHT was investigated. BHT is used as an antioxidant in food, in petroleum products, synthetic rubbers, plastics, etc. Free radicals are very reactive species characterised by unpaired electron. These radicals initiate a chain reaction, reacting many times until the chain is terminated by electron pairing. Free radicals can be formed by thermal cleavage of a hydrocarbon chain or hydrocarbon reaction with oxygen or light. The phenolic free radical of BHT forms an inactive dimer or reacts much faster with free radicals, terminating the chain (66).

The effect of BHT on naphthalene destruction was examined. Naphthalene contaminated organic soil 200 g was milled for 30, 60, 90 and 120 minutes. The milling was done in two batches one with addition of 4 g of BHT and the other one without addition of BHT.

2.4.4 Anthracene destruction with and without BHT

100 g of each soil (scoria and silica sand) contaminated with anthracene (section 2.3.2) was milled for 30, 60, 90 and 120 minutes. Milling was done in two batches for each type of soil, one with addition of 2 g of BHT and the other one without addition of BHT.

2.4.5 Phenanthrene destruction with and without BHT

100 g of each soil (scoria and silica sand) contaminated with phenanthrene (section 2.3.3) was milled for 30, 60, 90 and 120 minutes. Milling was done in two batches for each type of soil, one with addition of 2 g of BHT and the other one without addition of BHT.

2.4.6 Phenanthrene destruction with paraffin wax

Near the end of this study it became clear that the presence of substances that could lubricate or similarly, affect the ball impacts in the milling process. Paraffin wax was used to test this.

100 g of scoria contaminated with 0.25 g of phenanthrene was milled for 0, 30, 60 and 90 minutes. Milling was done in two batches, one with addition of 2 g paraffin wax and the other one with addition of 4 g paraffin wax

2.4.7 Hydrocarbon destruction with and without BHT

200 g of soil contaminated with long chain hydrocarbons (section 2.3.4) was milled for 30, 60, 90 and 120 minutes. Milling was also done in two batches, one with addition of 4 g of BHT and the other one without addition of BHT.

2.4.8 Hydrocarbon and Aluminium

200 g of soil contaminated with long chain hydrocarbons (section 2.3.4) was milled for 30, 60, 90, 120, 150 and 180 minutes with the addition of 20 g aluminium metal.

Aluminium is soft and easily forms fresh metal surfaces during milling. Fresh metal surfaces have the potential to be catalytic to either enhance or inhibit radical reactions.

2.4.9 Change of sample volume to be milled

50 g of scoria and 50 g of slag both contaminated with n-octacosane was milled for 30, 90, 120 and 180 minutes in order to observe the effect of sample mass used for milling. Slag is highly alkaline and was used in order to observe the effect of alkaline soil in the mechanochemical reaction.

2.5 EXTRACTION PROCEDURES

EPA Ultrasonic extraction method (METHOD 3550C) (67) was used for all analyses.

A summary of the method is:

1. Weigh 2 g of ground (treated) sample directly into test tube.
2. Add 10mL of Hexane extractant containing internal standard.
3. Shake vigorously by hand to mix the extractant and soil.
4. Place the tubes in a sonicator for 15 minutes at 15°C. Once the sonication has finished centrifuge at 2000rpm for five minutes.
5. Inject sample on the GC
6. Repeat step 1-6 for spiked unground (untreated) sample to obtain initial concentration before destruction process.

2.6 ANALYSIS

Samples were either analysed using GC with FID detector or mass spectrometric detector.

2.6.1 Naphthalene

For each sample analysis was done by GC/FID using DB-1 column. The temperature program was isothermal 150°C column temperature, 260°C detector temperature and 260°C injector temperature, split injection with a 20:1 split analysis. The carrier gas nitrogen flow rate was 20mL/min.

3µL sample of extract which contained internal standard were manually injected. N-tridecane had retention time of around 2.6 minutes and naphthalene 5.6 under these conditions. The following is an example of a chromatogram obtained during the analysis.

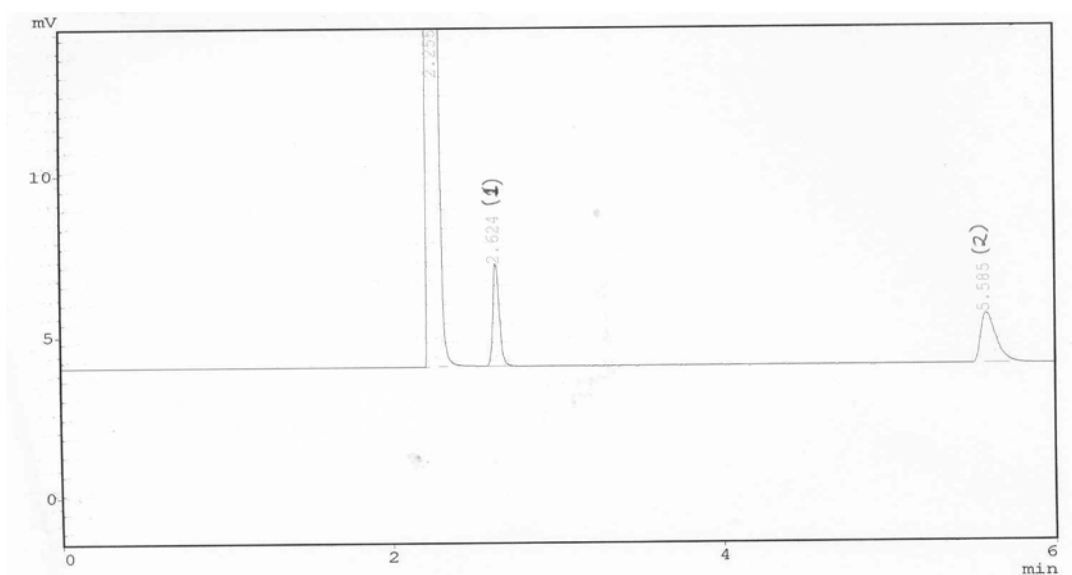


Figure 2.1: Example of chromatogram for naphthalene.

Peak (1): Internal standard n-tridecane; Peak (2): Naphthalene

2.6.2 Anthracene and Phenanthrene

Each sample was analysed by GC-MS using DB-5 column. The temperature program was isothermal 200°C column temperature, 260°C detector temperature and 260°C injector temperature, split injection with a 20:1 split analysis. The flow rate was 20mL/min.

1µL sample of extract which contained internal standard were manually injected. n-tridecane had retention time of around 2.2 minutes and both anthracene and phenanthrene had retention times of around 5.6 minutes under these conditions.

2.6.3 Aliphatic hydrocarbons

For long chain hydrocarbons, the GC/FID column, injector and detector temperatures were increased to 200°C, 300°C and 300°C respectively. The carrier gas flow rate remained the same at 20mL/min.

During the study a new column DB-5 was used with different specifications which led to changes of some experimental conditions. For long chain hydrocarbons, the column temperature had to be changed to 300°C and 350°C for injector and detector. For PAH there were no changes in operating temperature, however naphthalene was observed to come out first instead of the internal standard as observed in the previous column DB-1.

An example of a typical chromatogram obtained for aliphatic hydrocarbons is presented below.

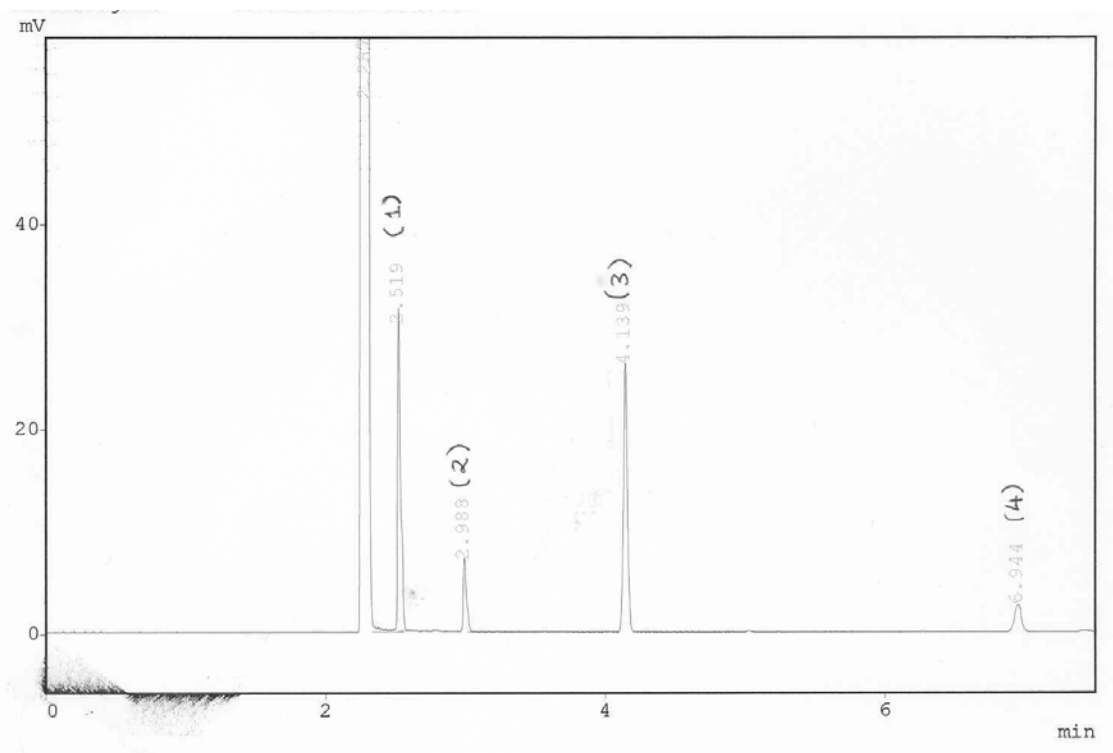


Figure 2.2: Example of chromatogram for aliphatic hydrocarbons.

Peak (1): BHT; Peak (2): n-eicosane; Peak (3): Internal standard n-tetracosane; Peak (4): n-octacosane.

2.7 DATA ANALYSIS

Concentrations of analytes were determined by calculating the ratios of peak areas divided by the area of the internal standards. Using the standard solutions curves, the residual concentration in the soil was determined.

CHAPTER 3

3.0 RESULTS

3.1 CALIBRATION STANDARDS

3.1.1 PAHs calibration standards

3.1.1.1 Naphthalene

Naphthalene standard solutions of 5000, 2000, 1000, 500 and 100 ppm were prepared. 1 μ L of each sample was injected into the GC-FID. The peak area obtained is presented in table 3.1. Figure 3.1, shows the standard curve obtained from the data.

Table 3.1: Results of naphthalene standard solutions

Naphthalene concentration (ppm)	Area ratio
5000	11.65
2000	4.49
1000	2.39
500	1.11
100	0.27

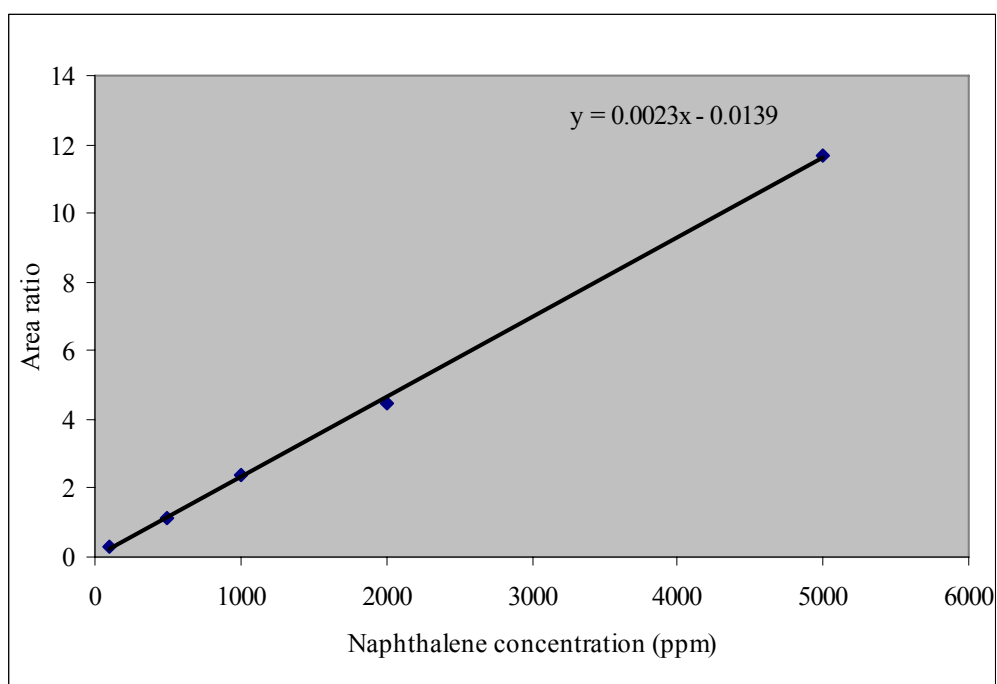


Figure 3.1: Naphthalene standard curve

3.1.1.2 Anthracene

Anthracene standard solutions of 2000, 1000, 500, 200 and 100 ppm were prepared. 1 μ L of each sample was injected into the GC-MS, the results obtained are presented in table 3.2. Figure 3.2, shows the standard curve obtained from the data.

Table 3.2: Results of anthracene standard solutions

Anthracene concentration (ppm)	Area ratio
2000	4.1
1000	2.1
500	1.1
200	0.5
100	0.2

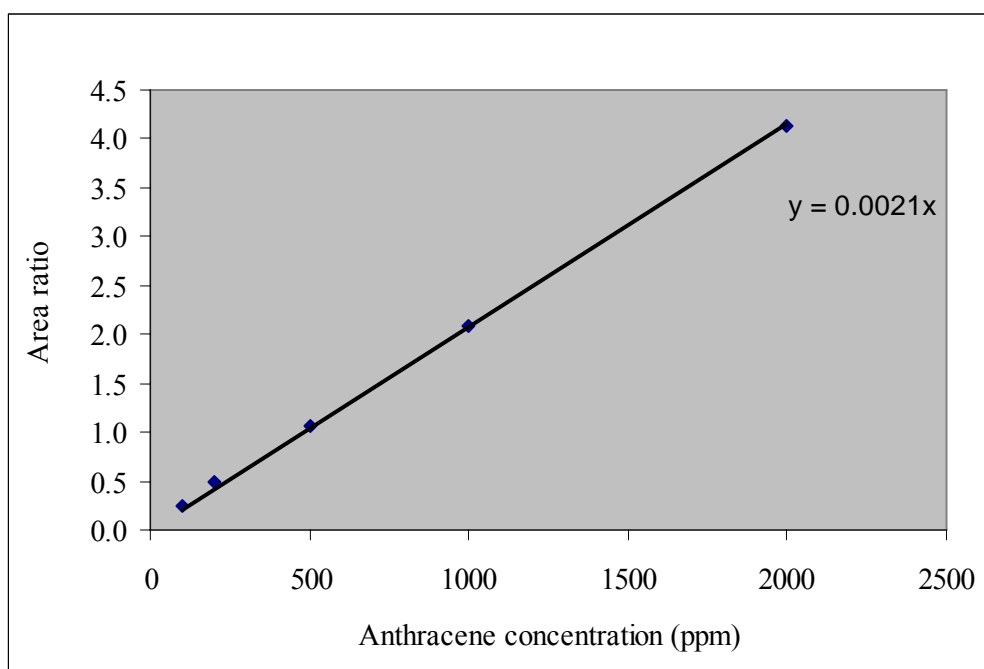


Figure 3.2: Anthracene standard curve

3.1.1.3 Phenanthrene

Phenanthrene standard solutions of 1000, 500, 250, 125 and 64 ppm were prepared, 1 μ L of each sample was injected into the GC-MS, and the results obtained are presented in table 3.3 below. Figure 3.3, shows the standard curve obtained from the data

Table 3.3: Results of phenanthrene standard solutions

Phenanthrene concentration (ppm)	Area ratio
1000	2.8
500	1.6
250	0.8
125	0.4
64	0.3

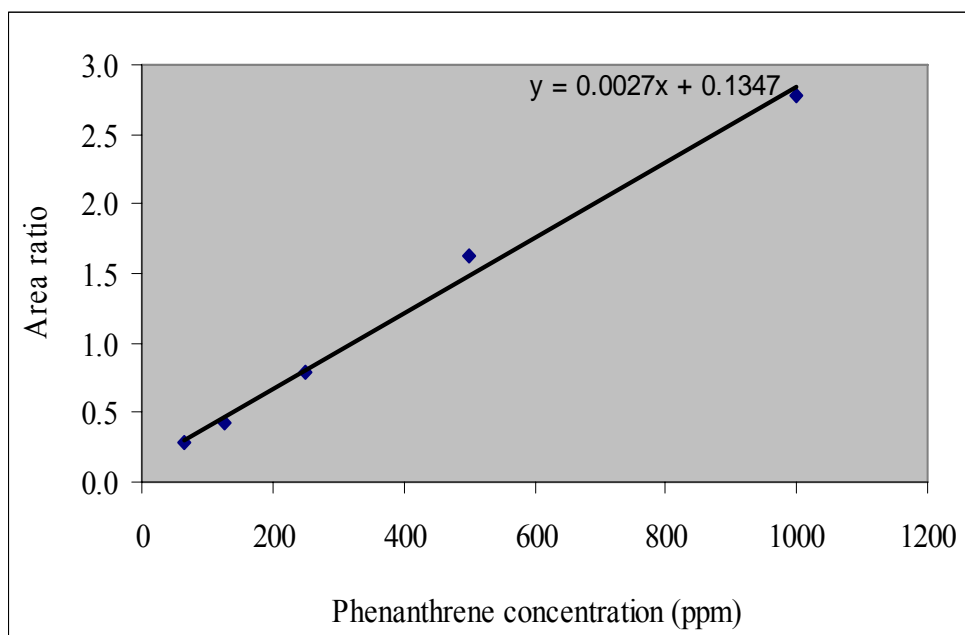


Figure 3.3: Phenanthrene standard curve

3.1.2 Aliphatic hydrocarbons calibration standards

For Long chain hydrocarbons, 1 μ L of n-eicosane and n-octacosane standard solutions of concentration 10000, 5000, 2000, 1000 and 500 ppm were prepared, 1 μ L of each sample was injected into the GC-MS, and the results obtained are presented in table 3.4 and 3.5 respectively. The standard curve area is presented in figure 3.4 and 3.5.

Table 3.4: Results of n-eicosane standard solutions

Eicosane concentration (ppm)	Area ratio
10000	2.12
5000	1.14
2000	0.49
1000	0.37
500	0.20

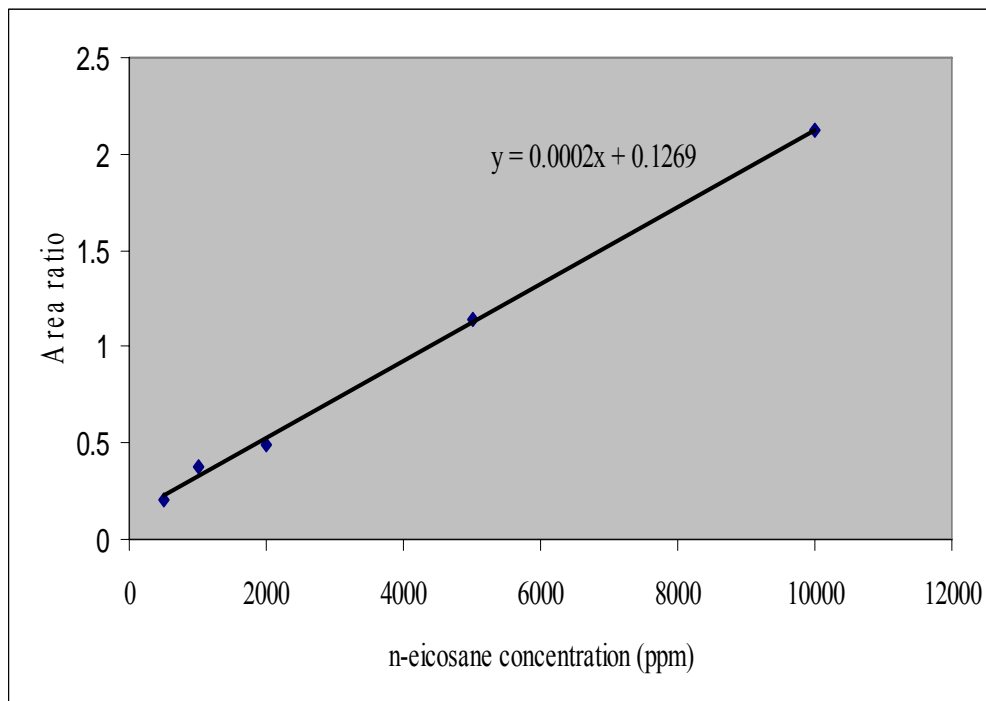


Figure 3.4: n-eicosane standard curve

Table 3.5: Results of n-octacosane standard solutions

Octacosane concentration (ppm)	Area ratio
10000	1.61
5000	0.91
2000	0.36
1000	0.16
500	0.09

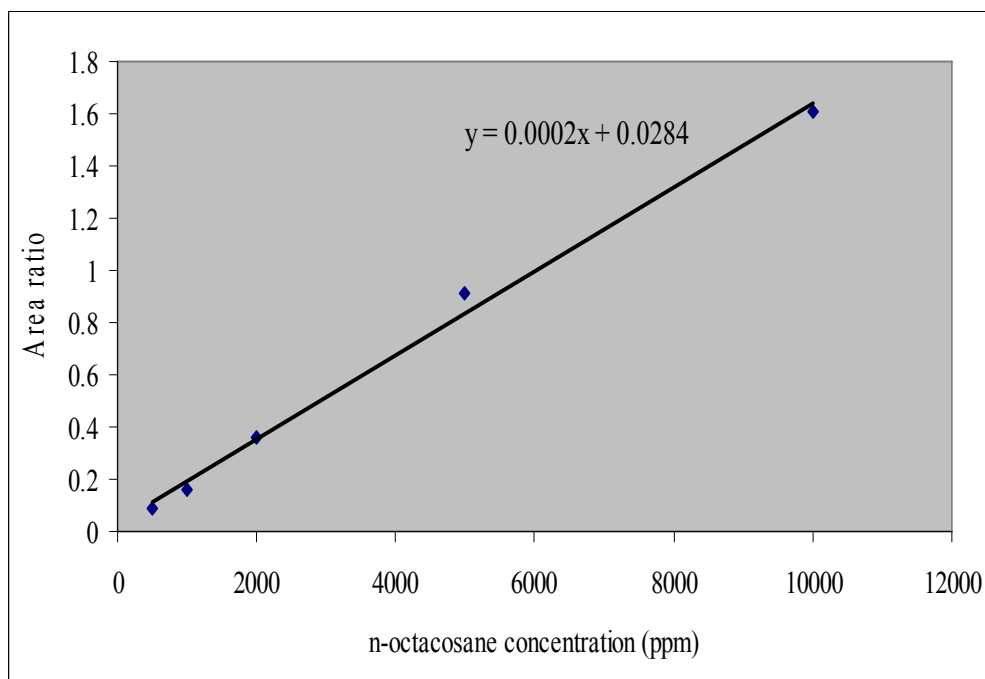


Figure 3.5: n-octacosane standard curve

From the above graphs (figure 3.1-3.5) the results of standard solutions of both PAH's and aliphatic hydrocarbons showed good linearity.

3.2 VOLATILIZATION CHECK FOR NAPHTHALENE

Naphthalene is a fairly volatile solid and there was concern that it could migrate from the soil matrix to the walls of the container as the soil heated up during the milling procedure.

Therefore, as stated in chapter 2, volatilization experiments were conducted using two different procedures. Procedure one involved 2500 ppm naphthalene contaminated soil. Samples were taken from the sealed milled after being milled for 2 minutes to give an homogeneous sample and placed the sealed jar in oven at 100°C for 30 minutes. There results are shown in tables 3.6a and 3.6b.

Table 3.6a: Results of naphthalene volatilization procedure 1.

Sample	Concentration (ppm)
1	2500
2	2500
3	2578
4	2500

The results in table 3.6a show that there was no volatilization of naphthalene in the whole process of milling and extracting the naphthalene from the soil for analysis. In procedure two of the volatilization experiments on naphthalene evaporation, the naphthalene contaminated soil (2000 ppm) was left uncovered for several hours in a fume hood. Samples for analysis were taken after 2, 3, 5, 6, 36 and 72hrs. Results are shown in table 3.6b.

Table 3.6b: Results of naphthalene volatilization procedure 2.

Sample	Hours taken	Concentration (ppm)
1	2	2000
2	3	2000
3	5	1943
4	6	1886
5	36	nd
6	72	nd

Table 3.6b clearly shows the volatility of naphthalene and confirms that if the soil sample contaminated with naphthalene and be left for more than 36 hours without being covered, naphthalene will be lost by evaporation. Since samples taken after 36 hours,

naphthalene was not detected. This emphasises that care must be taken with sampling and storage of the contaminated soils.

3.3 DIFFERENT BALL TO SOIL RATIOS

For these experiments, 4 different batches of 100 g of naphthalene contaminated scoria soil were milled with different number of balls; 20 balls, 10 balls, 5 balls and 1 ball. The milling was done at the standard speed of 500rpm for 30, 45, 60, 120 and 150 minutes. Results are presented in table 3.7.

Table 3.7: Naphthalene destruction in scoria soil milled with different ball to soil ratio

Milling time (minutes)	Naphthalene in soil (ppm)	Destruction efficiency (%)
20 balls		
0	680	0
30	270	60
60	225	67
90	105	85
120	50	93
150	0	100
10 balls		
0	680	0
30	365	47
60	290	57
90	255	63
120	135	80
150	105	85

5 balls		
0	680	0
30	590	14
60	520	24
90	305	56
120	235	66
150	170	75
1 ball		
0	680	0
30	575	15
60	560	17
90	325	52
120	275	59
150	185	73

In table 3.7, it was observed that the ball ratios have surprisingly little effect on the destruction efficiency of naphthalene in scoria soil. Milling results with 20 balls showed slightly higher destruction efficiency compared to 10, 5 and 1 ball milling. However, the destruction efficiency decreased with decreasing numbers of balls. Destruction efficiency obtained from 20 balls after milling for 150 minutes was 100%, for 10 balls 85%, for 5 balls 75% and for 1 ball was 73%. While it was not possible to change the size or geometry of the mill this result should be further investigated if a different design of mill is available.

These results are shown graphically in figure 3.6. It can be clearly seen that the 20 balls milling gives higher naphthalene destruction efficiency than the other experiments with 10, 5 and 1 ball.

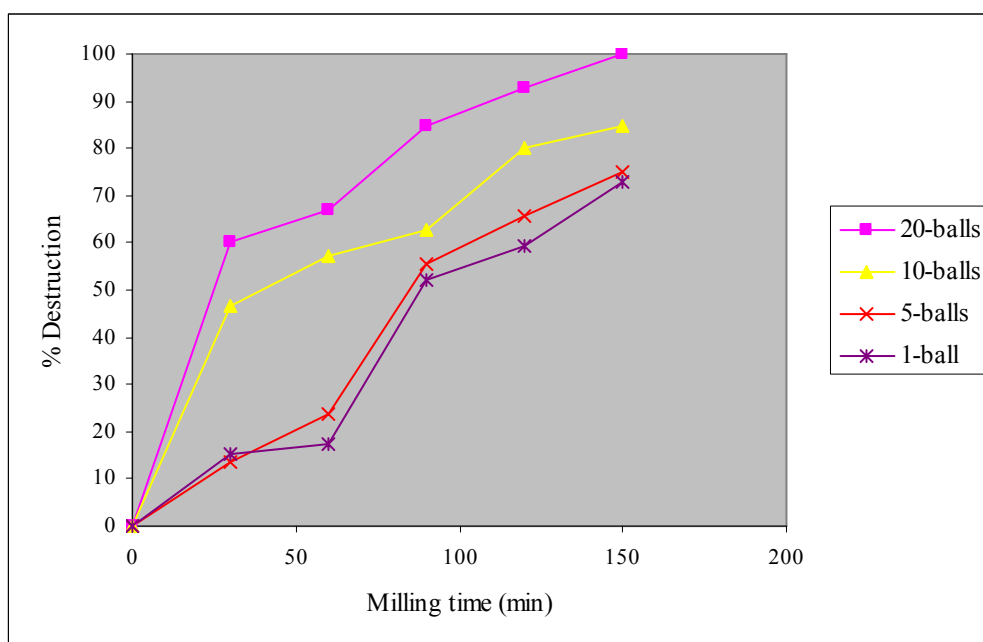


Figure 3.6: Naphthalene destruction in scoria soil with different ball to soil ratio

3.4 DIFFERENT SOIL TYPE

For these experiments, 4 different batches of 100 g of naphthalene contaminated clay soil were milled with different number of balls; 20 balls, 10 balls, 5 balls and 1 ball. The milling was done at 500 rpm for 30, 45, 60, 120 and 150 minutes. The results are presented in table 3.8.

Table 3.8: Naphthalene destruction in clay soil milled with different ball to soil ratio.

Milling time (minutes)	Naphthalene in soil (ppm)	Destruction efficiency (%)
20 balls		
0	675	0
30	605	10
60	560	17
90	415	38
120	260	61
150	160	76

10 balls		
0	675	0
30	630	7
60	535	21
90	440	35
120	335	50
150	290	57
5 balls		
0	675	0
30	660	2
60	640	5
90	550	18
120	545	19
150	500	25
1 ball		
0	675	0
30	665	1
60	650	4
90	640	5
120	635	6
150	600	11

These results are shown graphically in figure 3.7. It can be clearly seen that for the clay soil the 20 balls milling also gives slightly higher naphthalene destruction efficiency.

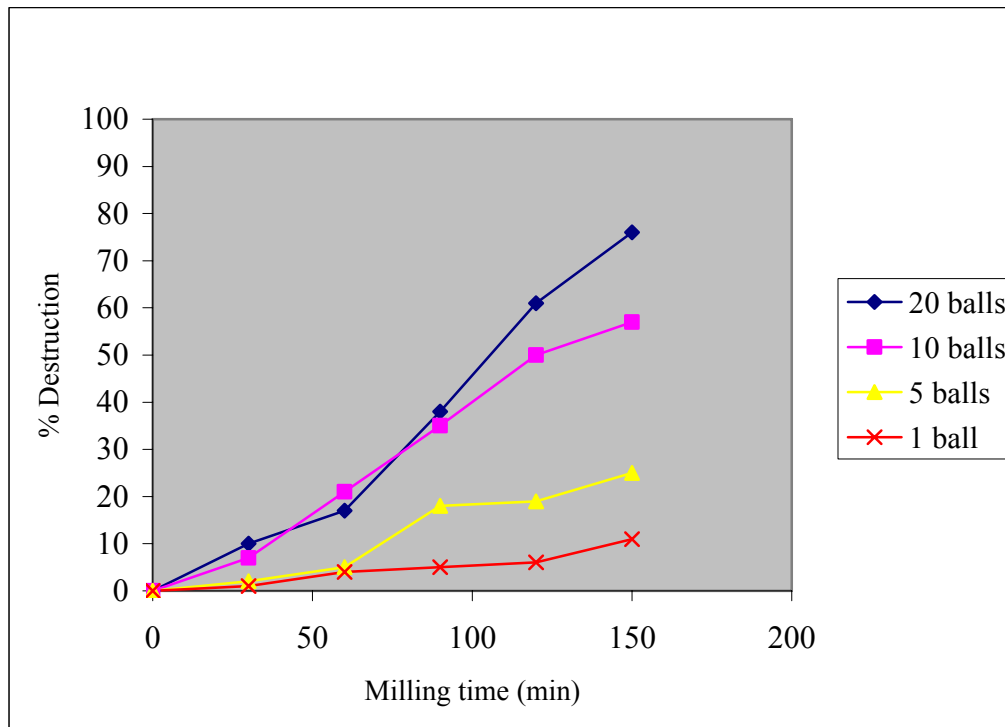


Figure 3.7: Naphthalene destruction in clay soil with different ball to soil ratio

As noted earlier, the ball to soil ratio in scoria has less of an effect than could be expected. However, the results of clay soil show a much more pronounced effect. Generally the results for the destruction of naphthalene in clay soil (table 3.8) showed a similar trend with that of the scoria (table 3.7). The destruction efficiency was decreasing with the decreasing number of balls. It is surprising to see in table 3.7 that even milling with 1 ball for 150 minutes gives 73 percent destruction. This suggests that some of the naphthalene was evaporating during milling process. However, none was observed during the milling and previous tests have shown that evaporation is not significant in the milling process (refer to section 3.2). It can be seen in table 3.8 that the clay soil milled for 150 minutes with 1 ball gave only 11 percent destruction. It could have been higher percent than that if evaporation of Naphthalene was significant.

3.5 NAPHTHALENE DESTRUCTION WITH AND WITHOUT ADDITION OF BHT

As stated in chapter 2, it is thought that the mechanism involved in ball milling is formation of free radicals. These experiments were conducted to check the effect of the radical inhibitor (BHT) in the destruction efficiency. 200 g of naphthalene contaminated organic soil were milled for 30, 60, and 90 minutes. The milling was done in two batches one with addition of 4g of BHT and the other one without addition of BHT. Thereafter the effect of BHT on naphthalene destruction was examined. Results for the destruction of naphthalene with BHT are presented in table 3.9 and without BHT are presented in table 3.10.

Table 3.9: Naphthalene destruction in organic soil milled with addition of BHT

Milling time (minutes)	Naphthalene in soil (ppm)	Destruction efficiency (%)
0	1305	0
30	1220	6
60	1180	10
90	1130	13

Table 3.10: Naphthalene destruction in organic soil milled without addition BHT

Milling time (minutes)	Naphthalene in organic soil (ppm)	Destruction efficiency (%)
0	1160	0
30	1120	9
60	1050	15
90	880	24

Table 3.9 and 3.10 shows the effect of adding BHT during the milling process. Results obtained showed that BHT reduces the destruction efficiency of the sample. Soil milled after 90 minutes without the addition of BHT gave 24 percent destruction while soil milled with BHT gave 13 percent destruction. Figure 3.8 below clearly shows the difference between using the radical inhibitor (BHT) in the mechanochemical reaction.

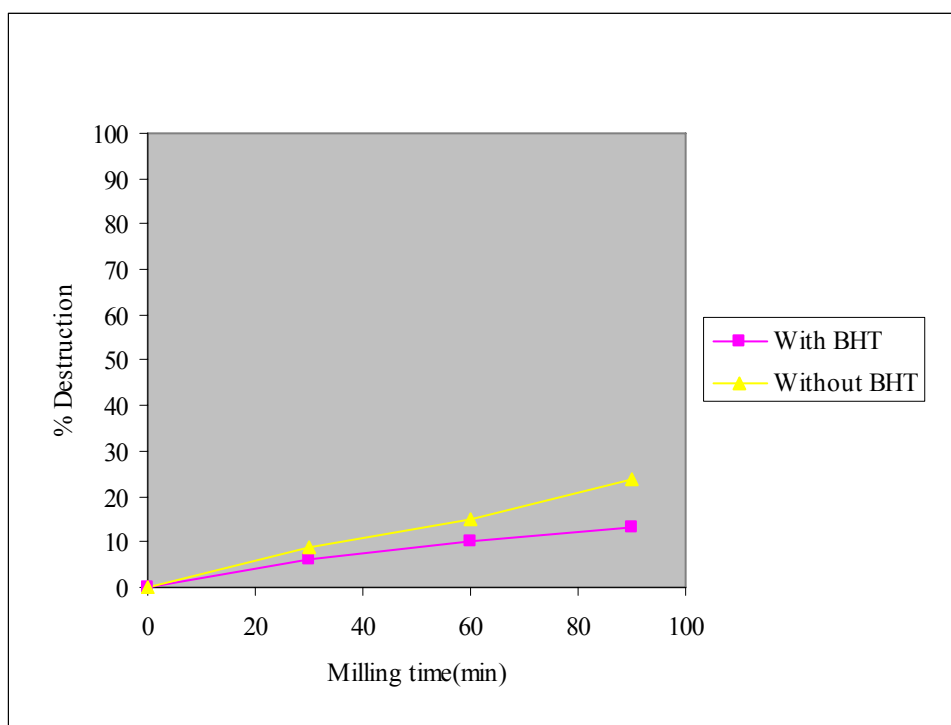


Figure 3.8: Naphthalene destruction with and without BHT in organic soil

However, naphthalene destruction in organic soil without BHT (table 3.10) was low compared to naphthalene destruction obtained in scoria and clay soil after 90 minutes with 20 balls, refer table 3.7 and 3.8 respectively, it is assumed that the presence of organic substances in the organic reach soil may have a competition with the naphthalene in the mechanochemical reaction.

3.6 ANTHRACENE DESTRUCTION WITH AND WITHOUT BHT

100g of scoria contaminated with anthracene was milled for 30, 60, 90 and 120 minutes. Milling was done in two batches; one with addition of 2g of BHT and the other one

without addition of BHT. The results are presented in table 3.11 and 3.12. The same experiment was conducted using silica sand.

Table 3.11: Anthracene destruction in scoria milled with addition BHT

Milling time (minutes)	Anthracene in scoria soil (ppm)	Destruction efficiency (%)
0	2341	0
30	2206	6
60	2137	9
90	1564	33
120	1214	48

Table 3.12: Anthracene destruction in scoria milled without addition of BHT

Milling time (minutes)	Anthracene in scoria soil (ppm)	Destruction efficiency (%)
0	2341	0
30	1500	36
60	585	76
90	110	95
120	0	100

Tables 3.11 and 3.12 show the effect of adding BHT during milling process. The results obtained showed that BHT reduces the destruction efficiency of the contaminant. Contaminated scoria milled after 120 minutes without addition of BHT gives 100 percent destruction while the same sample milled with BHT gave 48 percent destruction. The difference in the destruction efficiency can be clearly seen in Figure 3.9 below.

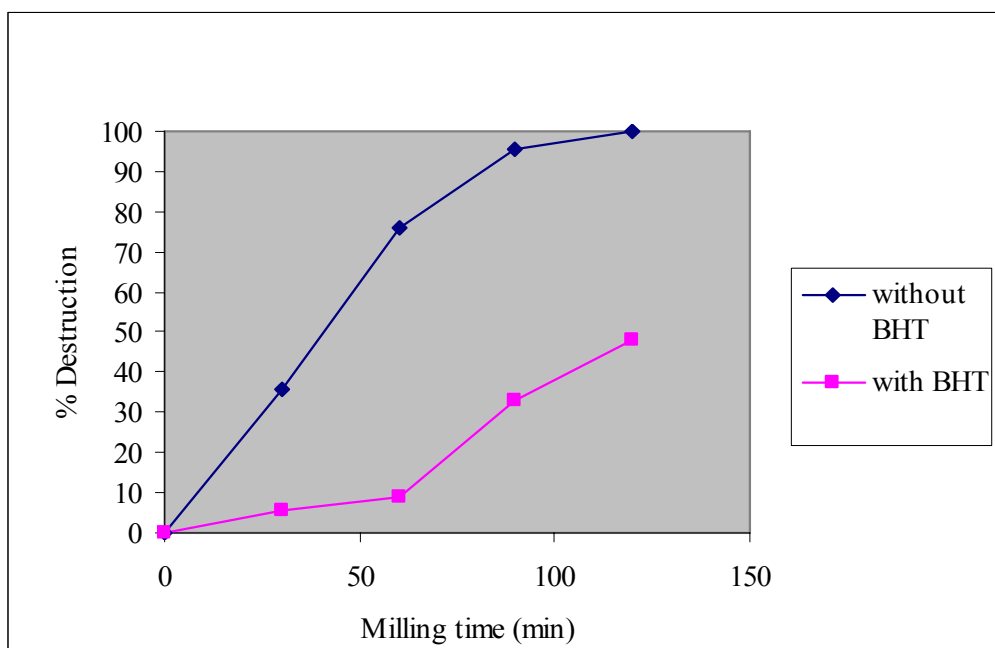


Figure 3.9: Anthracene destruction with and without BHT in scoria soil.

The experiment was repeated using anthracene in silica sand. The effect of BHT can also be seen in tables 3.13 and 3.14 below. The results showed that without BHT 100% destruction efficiency was achieved after 60 minutes (table 3.14), while for the same experiment in which BHT was added, milling done for 120 minutes gave only 34% destruction (table 3.13). Figure 3.10 shows the comparison of the results of these two experiments.

Table 3.13: Anthracene destruction in silica sand milled with addition BHT

Milling time (minutes)	Anthracene in silica sand (ppm)	Destruction efficiency (%)
0	2235	0
30	1962	12
60	1951	13
90	1605	28
120	1478	34

Table 3.14: Anthracene destruction in silica sand milled without addition of BHT

Milling time (minutes)	Anthracene in silica sand (ppm)	Destruction efficiency (%)
0	2235	0
30	555	75
60	0	100
90	0	100
120	0	100

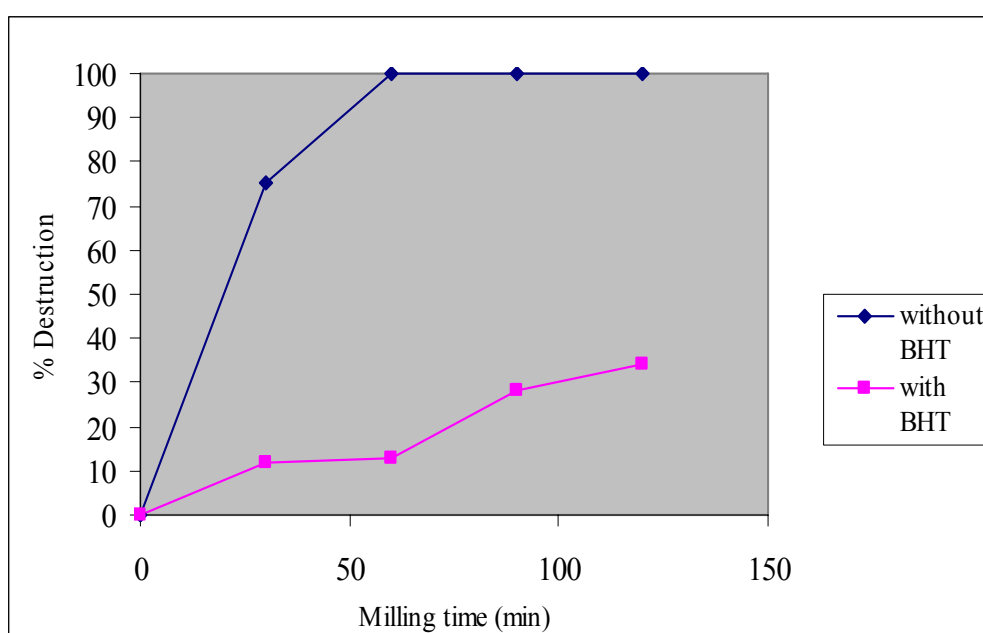


Figure 3.10: Anthracene destruction with and without BHT in silica sand.

A comparison of destruction efficiencies of anthracene in scoria soil and silica sand without addition of BHT gave the following results:

Table 3.15: Comparison of anthracene destruction in scoria and silica sand

Milling time (minutes)	Destruction efficiency in scoria soil	Destruction efficiency in silica sand
0	0	0
30	36	75
60	76	100
90	95	100
120	100	100

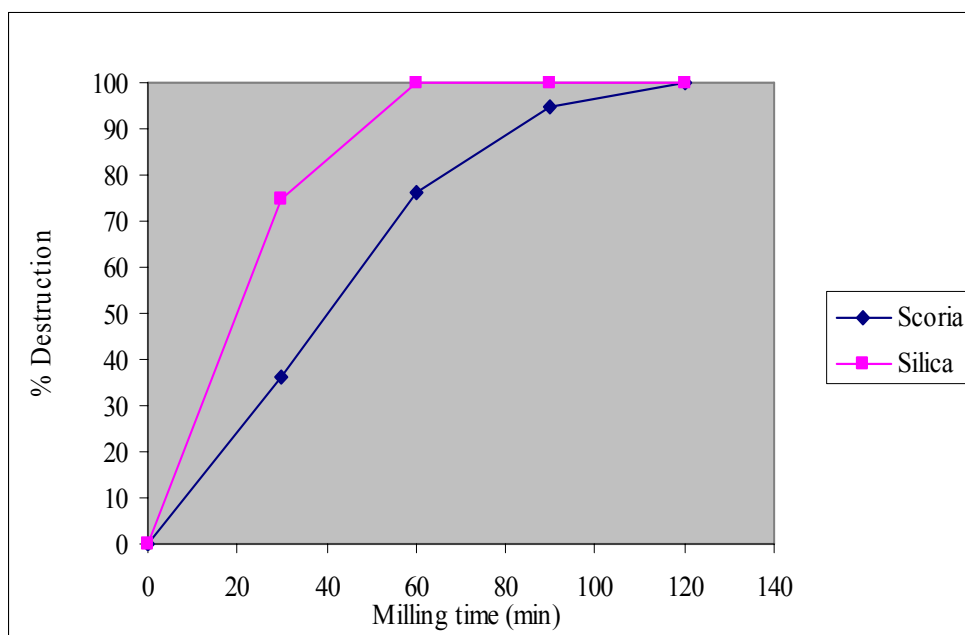


Figure 3.11: Comparison of anthracene destruction without BHT in scoria and silica sand.

It can be observed that, different type of soil clearly has an effect in the rate of destruction of anthracene. According to the results presented in table 3.15 it can be seen that, silica sand is the best in the mechanochemical reaction of anthracene. The destruction efficiency obtained from silica sand after milling the sample for only 60

minutes was 100%, while 100% destruction efficiency was obtained from the scoria soil after milling the sample for 120 minutes.

3.7 PHENANTHRENE DESTRUCTION WITH AND WITHOUT BHT

100 g of scoria contaminated with phenanthrene was milled for 30, 60, 90 and 120 minutes. Milling was done in two batches; one with addition of 2 g of BHT and the other one without addition of BHT. The results are presented in table 3.16 and 3.17.

Table 3.16: Phenanthrene destruction in scoria soil milled without addition of BHT

Milling time (minutes)	Phenanthrene in scoria soil (ppm)	Destruction efficiency (%)
0	2189	0
30	1584	28
60	1103	50
90	703	68
120	331	85

Table 3.17: Phenanthrene destruction in scoria soil milled with addition of BHT

Milling time (minutes)	Phenanthrene in scoria soil (ppm)	Destruction efficiency (%)
30	2427	0
60	2167	11
90	1982	18
120	1951	20

From table 3.16 and 3.17 above it can be seen that mechanochemical reaction can also be used to destroy phenanthrene. Results obtained showed that, as was the case for anthracene, BHT reduces the destruction efficiency of the sample. Soil milled for 120

minutes without addition of BHT gave 85% destruction while soil milled with BHT under similar conditions gave 20% destruction. Figure 3.12 below shows the difference between using and not using the BHT in the mechanochemical reaction.

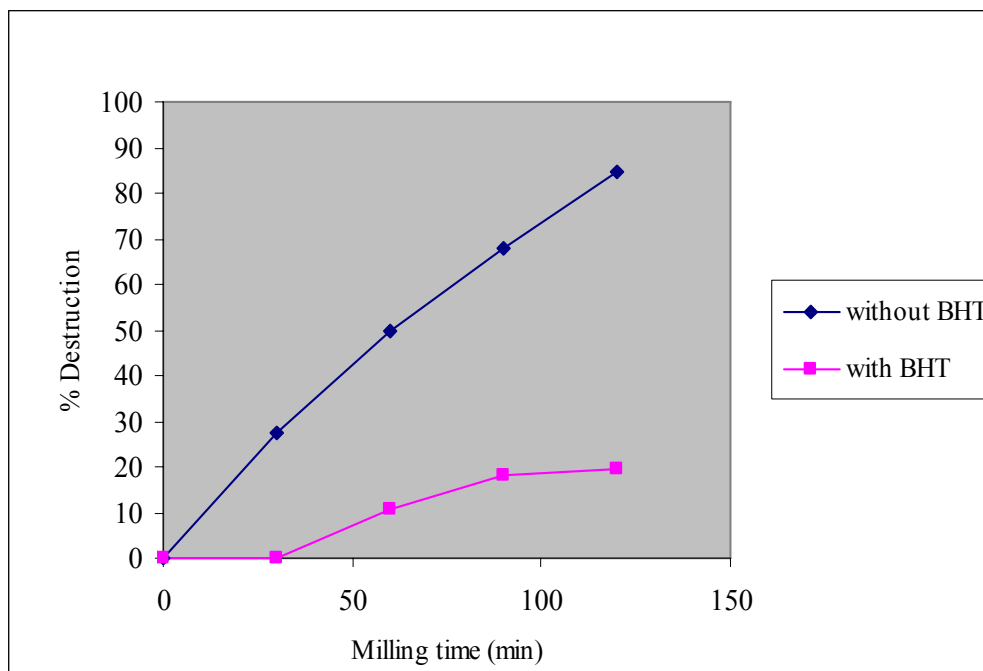


Figure 3.12: Phenanthrene destruction with and without BHT in scoria soil.

The destruction efficiency of phenanthrene in silica sand was determined (table 3.18 and 3.19) below. Similar results to those of anthracene were obtained. Contaminated silica sand milled without addition of BHT gave good results since milling 90 minutes was enough to achieve a destruction efficiency of 100%. This destruction efficiency was reduced upon addition of BHT. With the addition of BHT the destruction efficiency obtained after milling the sample for 120 minutes the destruction efficiency was only 12%, refer table 3.19. Comparison of the results of silica sand with and without BHT is plotted in figure3.13 below.

Table 3.18: Phenanthrene destruction in silica sand milled without addition of BHT

Milling time (minutes)	Phenanthrene in silica sand (ppm)	Destruction efficiency (%)
0	2252	0
30	1466	35
60	186	92
90	0	100
120	0	100

Table 3.19: Phenanthrene destruction in silica sand milled with addition of BHT

Milling time (minutes)	Phenanthrene in silica sand (ppm)	Destruction efficiency (%)
30	2268	0
60	2238	1
90	2105	7
120	1995	12

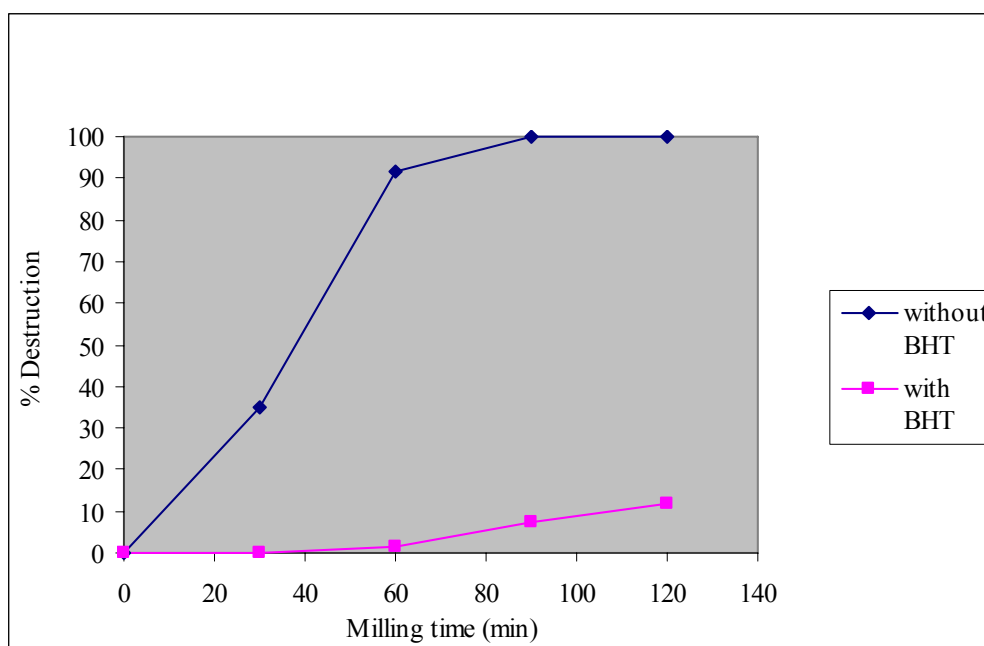


Figure 3.13: Phenanthrene destruction with and without BHT in silica sand.

The effect of soil type in phenanthrene destruction without addition of BHT was also noted. Results are presented in table 3.20 and the comparison can be seen in figure 3.14 below.

Table 3.20: Comparison of phenanthrene destruction in scoria and silica sand

Milling time (minutes)	Destruction efficiency in scoria soil	Destruction efficiency in silica sand
0	0	0
30	28	35
60	50	92
90	68	100
120	85	100

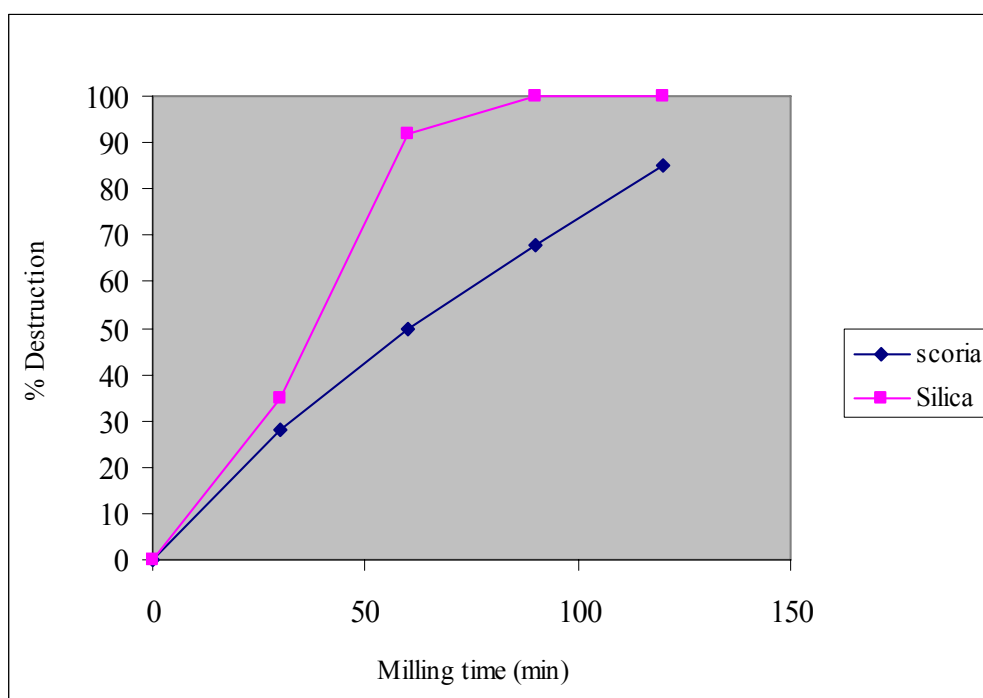


Figure 3.14: Comparison of phenanthrene destruction without BHT in scoria and silica sand.

From table 3.20 and figure 3.14 above, as with anthracene, silica sand is found to have better phenanthrene destruction efficiency compared to scoria soil. The destruction efficiency obtained from silica sand after milling the sample for 90 minutes was 100%, while 85% destruction efficiency was obtained from the scoria after milling the sample for 120 minutes.

3.8 COMPARISON OF THE THREE PAH's STUDIED

Comparison of all three PAH's; naphthalene, anthracene and phenanthrene were done. As it can be seen in the figure 3.15 below, they all have the same behaviour in the mechanochemical process. Naphthalene was expected to have a high destruction efficiency compared to anthracene and phenanthrene however the results did not support this expectation.

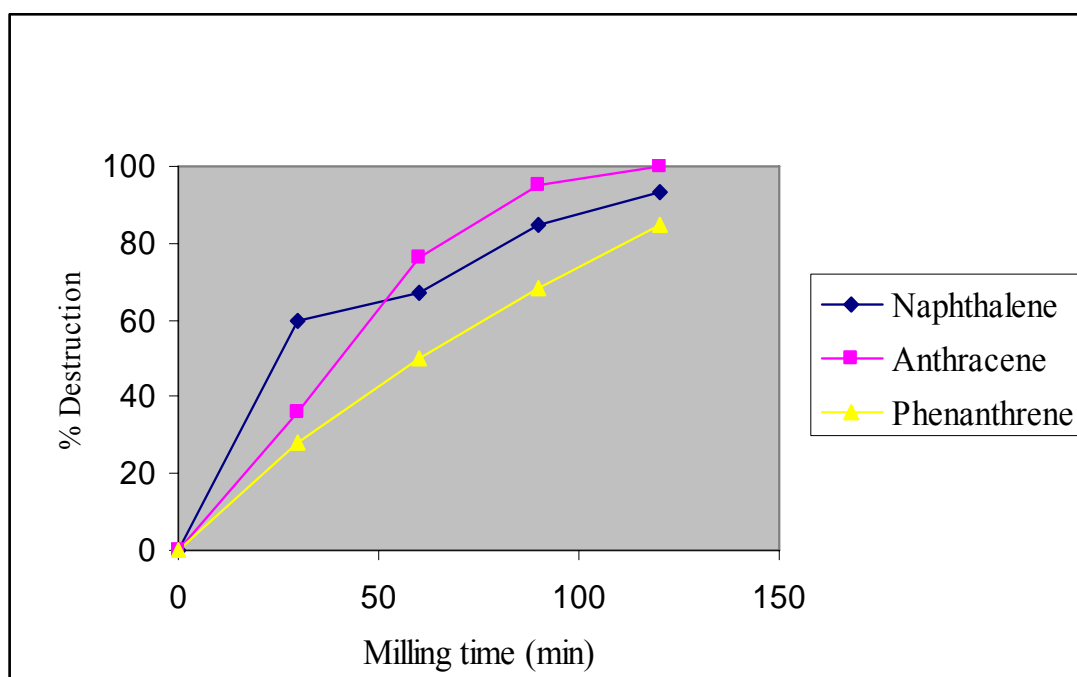


Figure 3.15: Comparison of naphthalene, anthracene and phenanthrene destruction in scoria soil.

3.9 PHENANTHRENE DESTRUCTION WITH ADDITION OF PARAFIN WAX.

During milling of phenanthrene with addition of BHT in above experiments, the soil was observed to have a greasy like formation. Based on the sound of the mill it was suspected that milling efficiency was also reduced. This was expected to affect the destruction process as the balls impacts will be reduced. Therefore, the destruction of phenanthrene with addition of parafin wax was investigated to see whether the presence of wax in the soil affected the destruction process.

100 g of scoria contaminated with 0.25 g of phenanthrene was milled for 0, 30, 60 and 90 minutes. Milling was done in two batches, one with addition of 2 g parafin wax and the other one with addition of 4 g paraffin wax. Results are shown in table 3.21 below. These results are shown graphically in figure 3.16 below.

Table 3.21: Phenanthrene destruction in scoria with addition of parafin wax

Milling time (min)	0 % wax	2 % wax	4 % wax
0	0	0	0
30	28	10	1
60	50	19	9
90	68	31	9

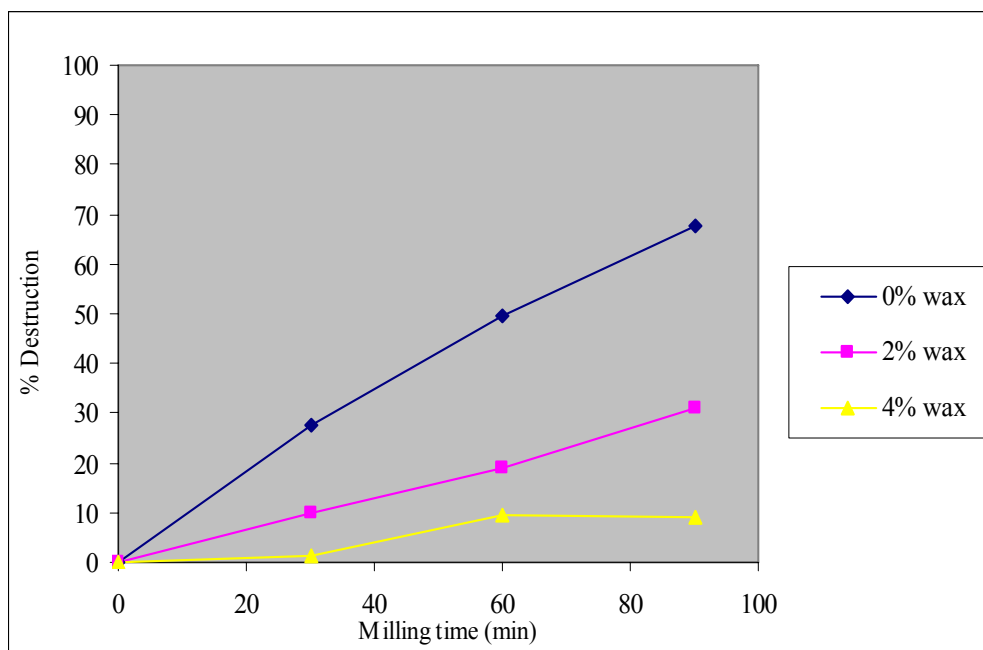


Figure 3.16: Comparison of phenanthrene destruction with addition of wax in different ratios.

From the above graph, it is clearly seen that presence of wax in the soil has a considerable effect on the destruction efficiency. The higher the percentage of wax in the soil the lower the destruction efficiency achieved.

3.10 ALIPHATIC HYDROCARBONS DESTRUCTION WITH AND WITHOUT ADDITION OF BHT

200 g of scoria soil contaminated with ~5000 ppm of long chain hydrocarbons (n-eicosane and n-octacosane) was milled for 30, 60, 90 and 120 minutes. Milling was done in two batches; one with addition of 4 g of BHT and the other one without addition of BHT. Results of n-eicosane without and with addition of BHT are presented in table 3.22 and 3.23; and results of n-octacosane without and with addition of BHT are presented in table 3.24 and 3.25.

Table 3.22: n-eicosane destruction in scoria soil

Milling time (minutes)	n-eicosane in soil (ppm)	Destruction efficiency (%)
0	4775	0
30	4035	15
60	2815	41
90	1855	61
120	1775	63

Table 3.23: n-eicosane destruction in scoria soil milled with addition of BHT

Milling time (minutes)	n-eicosane in soil (ppm)	Destruction efficiency (%)
0	4775	0
30	3520	26
60	2930	38
90	2785	41
120	2560	46

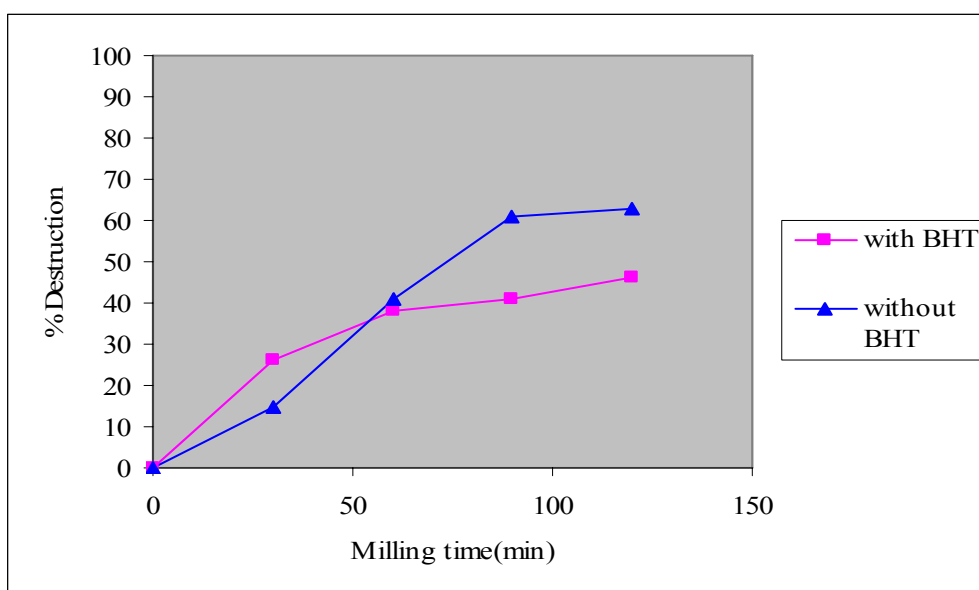


Figure 3.17: n-eicosane destruction with and without BHT in scoria soil.

From table 3.22 and 3.23, it can be seen that after milling the sample for 120 minutes, the sample which has no BHT had higher destruction efficiency of 63% compared to 46% destruction for the sample milled together with BHT.

Table 3.24: n-octacosane destruction in scoria soil

Milling time (minutes)	n-octacosane in soil (ppm)	Destruction efficiency (%)
0	4355	0
30	3630	17
60	3485	20
90	3355	23
120	3290	24

Table 3.25: n-octacosane destruction in scoria soil milled with addition of BHT

Milling time (minutes)	n-octacosane in soil (ppm)	Destruction efficiency (%)
0	4355	0
30	3950	9
60	3795	13
90	3765	14
120	3665	16

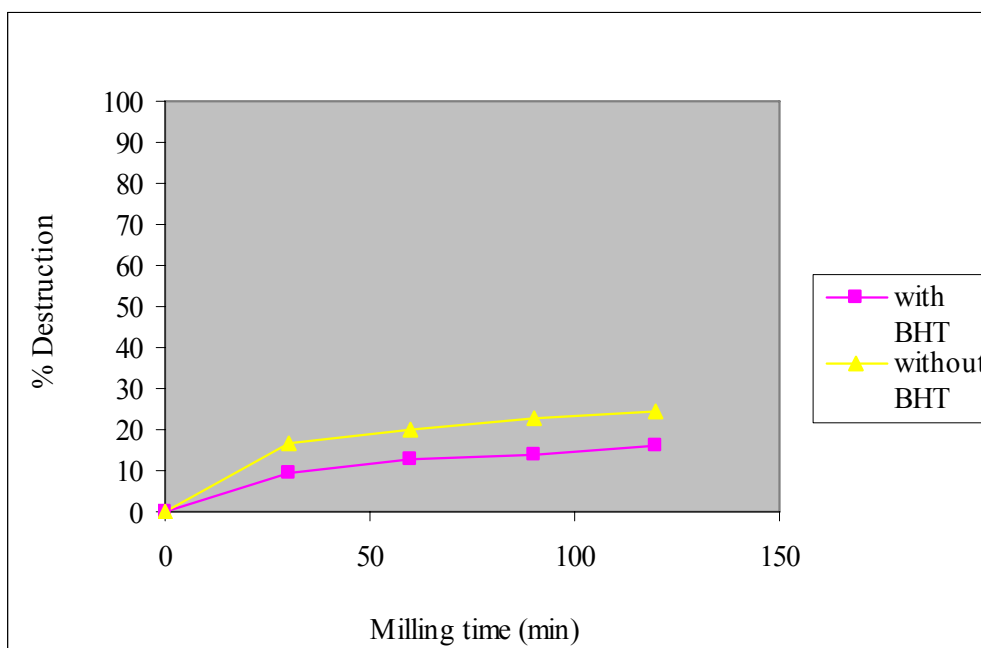


Figure 3.18: n-octacosane destruction with and without BHT in scoria soil.

Table 3.24 and 3.25 shows that n-octacosane was more difficult to destroy compared to n-eicosane. The average percent destruction of n-eicosane after being milled for 120 minutes (table 3.22 and 3.23) was about 55%, while for n-octacosane (table 3.24 and 3.25) was about 20%. However, for n-octacosane it showed that BHT also had an effect in its destruction rate since the percent destruction for the sample milled for 120 minutes showed that with 2% BHT the destruction efficiency was reduced from 24% to 16%.

The evidence that wax inhibit destruction efficiency was found after this work was completed. The waxy nature of these hydrocarbons may have an effect in the destruction process.

3.11 HYDROCARBON DESTRUCTION WITH ADDITION OF ALUMINIUM METAL

200 g of scoria soil contaminated with n-eicosane and n-octacosane was milled for 30, 60, 90, 120, 150 and 180 minutes with the addition of 20 g aluminium metal. Results are presented in table 3.26 for n-eicosane and table 3.27 for n-octacosane.

Table 3.26: n-eicosane destruction in scoria soil milled with addition of aluminium metal

Milling time (minutes)	n-eicosane in scoria soil (ppm)	Destruction efficiency (%)
0	4600	0
30	3625	21
60	3625	21
90	2825	39
120	2145	53
150	2140	53
180	1550	66

Table 3.27: n-octacosane destruction in scoria soil milled with addition of aluminium metal

Milling time (minutes)	n-octacosane in scoria soil (ppm)	Destruction efficiency (%)
0	4125	0
30	3450	16
60	3185	23
90	3145	24
120	3030	26
150	2700	35
180	2390	42

By comparing the results of table 3.26 (destruction of n-eicosane with aluminium metal) and that of table 3.22 (destruction of n-eicosane without aluminium metal), the destruction rate of n-eicosane after being milled for 120 minutes is 53% and 63% respectively. This showed there was little difference in destruction efficiency for n-eicosane alone or by adding aluminium metal during milling, though the destruction efficiency was reduced 10% for the sample milled with aluminium. In the case of n-octacosane, in table 3.27 (destruction of n-octacosane with aluminium metal) and 3.24

(destruction of n-octacosane without aluminium metal) the destruction efficiency of n-octacosane after being milled for 120 minutes is 26% and 24% respectively. This means that for n-octacosane the destruction efficiency increased by only 2%. This indicates that addition of aluminium does not have much effect in the destruction of long chain hydrocarbons particularly n-eicosane and n-octacosane used in these experiments.

Additionally it can be observed that n-octacosane was hard to destroy even after being milled for 180 minutes since the destruction efficiency obtained was only 42 % (table 3.27) while that of the n-eicosane was 66 % (table 3.26).

3.12 DESTRUCTION OF N- OCTACOSANE USING 50 g SOIL SAMPLE FOR MILLING

50 g of scoria soil contaminated with n-octacosane was milled at 30, 90, 120 and 180 minutes. This was done in order to find how the sample volume affects the destruction efficiency. Results are presented in table 3.28.

Table 3.28: n-octacosane destruction efficiency from milling 50 g scoria soil

Milling time (minutes)	n-octacosane in soil (ppm)	Destruction efficiency (%)
0	27018	0
30	24827	8
90	22949	15
120	22372	17
180	13951	48

Table 3.28 shows that n-octacosane was more difficult to destroy, as the results show reducing weight of soil sample for milling from 200 g to 50 g does not have much effect. The percent destruction obtained by milling 200 g of soil contaminated with n-octacosane for 120 minutes was 24% (table 3.24) while the percent destruction obtained after milling 50 g soil contaminated with n-octacosane for 120 minutes was only 17%

(table 3.28). Continuing milling of the same sample for 3 hours gave only 48% destruction. The low destruction efficiency obtained in this experiment may be due to the waxy greasy nature of the soil with 27,000 ppm n-octacosane reducing milling effectiveness. Since low destruction efficiency was also observed for the PAH's with the presence of paraffin wax, section 3.9.

Also slag was contaminated with n-octacosane and milled for 30, 90, 120 and 180 minutes. This was done in order to get comparison with scoria soil using only 50 g sample for milling. Results are presented table 16. Slag was used as another type of soil matrix

Table 3.29: n-octacosane destruction rate from milling 50 g slag

Milling time (minutes)	n-octacosane in soil (ppm)	Destruction rate (%)
0	28326	0
30	26266	7
90	25939	8
120	21855	23
180	19807	30

By comparing results of table 3.28 and table 3.29, it shows that n-octacosane was more easily destroyed in a scoria matrix rather than a slag matrix. Milling of the scoria contaminated with n-octacosane for 180 minutes gave 48 percent destruction while for the slag only 30 percent destruction occurred. The alkalinity of the slag did not improve the destruction process of n-octacosane.

CHAPTER 4

4.0 DISCUSSION

Having outlined the sources of chemical contaminants of soil and the destruction technologies used, it is now possible to discuss the aim and the achievement of this project. The aim of this project was to investigate the destruction or chemical transformations of selected classes of compounds in various soil matrices using a laboratory scale ball mill as a mechanochemical reactor.

The classes of compounds chosen were polycyclic aromatic hydrocarbons ((PAH's) and aliphatic hydrocarbons. Experiments were conducted using different milling parameters such as different soil type, different ball ratios, and different amount of soil to be milled. Some other experiments involve the addition of BHT or Aluminium metal.

So far, there does not seem to be a good agreement among the various authors on a theoretical basis of the reactive milling. Most published results (27, 59) have little detail on reaction mechanisms and intermediates and indeed it seems as though they are deliberately ignoring what seems to be a difficult and uncertain area. Where they are identified and discussed, the reactions seem to give a melange of products, reminiscent of uncontrolled free radical reactions such as the reaction of chlorine and methane gas where many possible combinations of the elements are formed.

However, it is known that during milling there is a high energy impact between surfaces of the balls which produces localised spots of very high energy (28). These high energy "hot spots" initiate the chemical reactions that can, ultimately, lead to the complete destruction of organic compounds in the mill. While milling is taking place there is deformation and fracture of the reactant particles which increases the activated surfaces, and continuously creates new surfaces to facilitate further decomposition reactions and eventually the destruction of chemical compounds (29).

4.1 DISCUSSION OF THE RESULTS

4.1.1 Different ball ratios

In chapter 3, section 3.3 results of different ball ratios using scoria soil (Table 3.7), shows that ball numbers have little effect on the percentage destruction. It can be observed that the higher the number of balls the higher the percent destruction obtained, refer figure 3.6, chapter 3. Though the effect was not much observed may be due to the short milling time of the experiment, this suggest that if the experiment was conducted for longer times there is a possibility that the effect of number of balls could be clearly noticed. The main reason for this phenomenon is because; higher number of balls provides more impacts per unit time (65) compared to few number of balls. And the greater the number of impacts the higher the energy produced, and more mechanochemical reactions are expected to take place, which will lead to higher percentage destruction. . But it is assumed that if milling was continued for longer all results would have reached 100% destruction.

There is no reason to suppose that the destruction may have occurred due to thermal breakdown of the compounds. Although the mill gets hot during milling, the surface temperature of the mill was occasionally measured using thermocouple and was found to be about 90°C. The compounds used are completely stable at this temperature and for the 3 hours or less used in the experiments.

4.1.2 Different soil type

Comparing the results obtained with scoria and clay soil (table 3.7 and table 3.8 respectively), in general it can be observed that the results have similar trend. In both soils the percentage destruction decreased with decreasing number of balls which will reduce the total amount of energy. However for scoria soil there was not much difference in percentage destruction with different number of balls as compared to the clay soil. Also, the total percentage destruction of the scoria soil was much higher than the clay soil for all experiments with similar ball numbers and milling times, see figures 4.1, 4.2, 4.3 and 4.4 below.

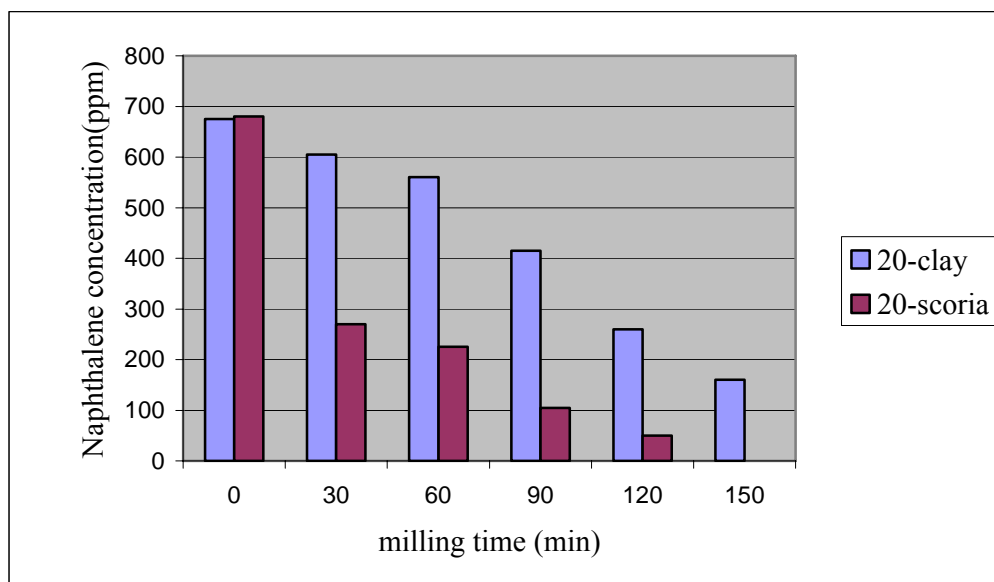


Figure 4.1: Comparison between scoria and clay soil milled with 20 balls at different time intervals

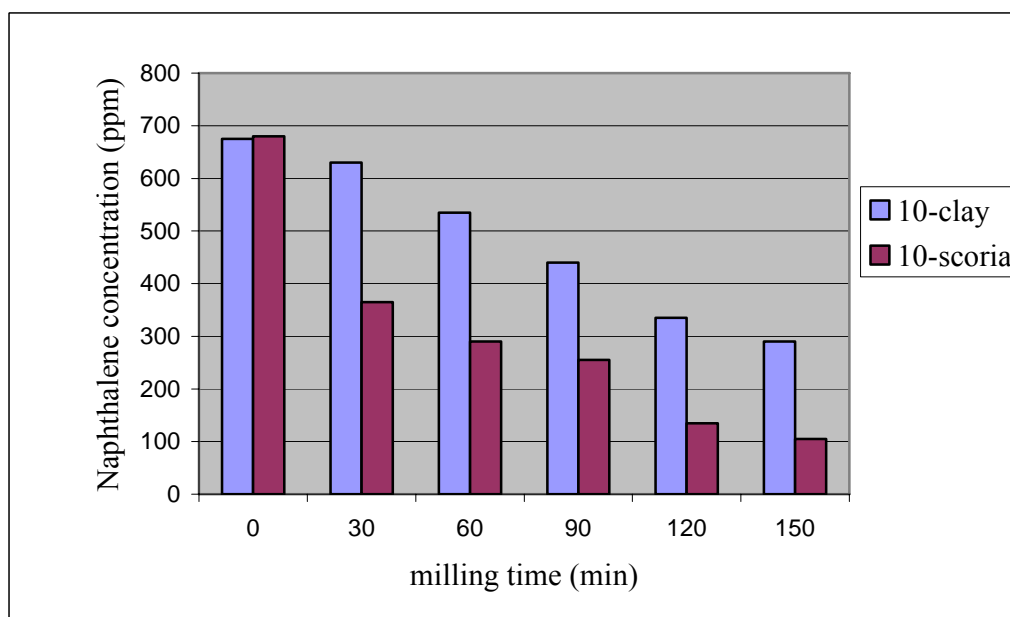


Figure 4.2: Comparison between scoria and clay soil milled with 10 balls at different time intervals

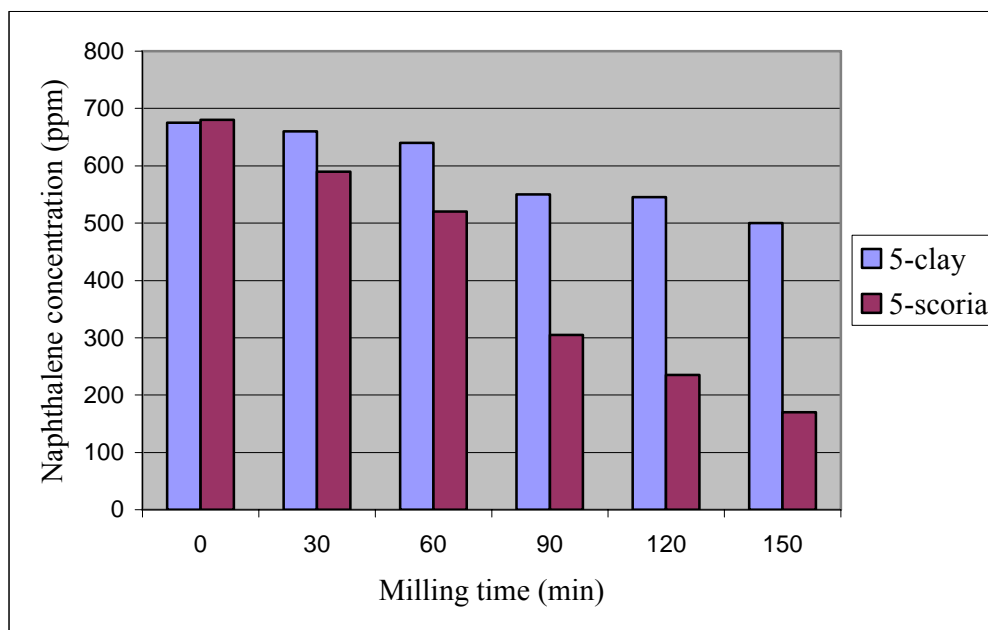


Figure 4.3: Comparison between scoria and clay soil milled with 5 balls at different time intervals

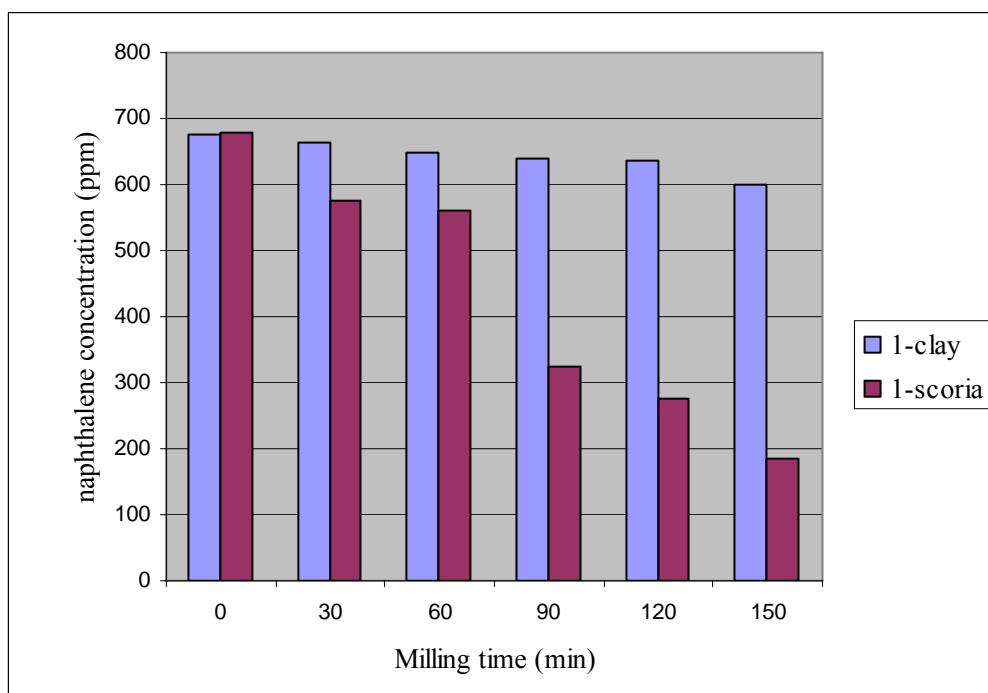


Figure 4.4: Comparison between scoria and clay soil milled with 1 ball at different time intervals

In Figures 4.1, 4.2, 4.3, and 4.4 above, it can be observed that the clay soil remain with higher naphthalene concentration than scoria soil in almost all the experiments with different ball ratios.

This suggests that different soil types behave differently in the mechanochemical reactions that occur during milling. This may possibly be due to energy transfer. Perhaps the energy transfer is very efficient; especially in the scoria soil so that once reaction is initiated it can spread through the mixture.

Also it is known that soil texture has a major effect on the physical and chemical characteristics of soil (68). Sandy soils have rather large particles and large pore space while clay soils have very small particles with small pore space, but because they are many times more pore spaces, clay soils have greater total pore space than sandy soils (68). Clay soils have better absorption and retain much more water than sandy soils (68) this may be the reason why it is not as easy to destroy naphthalene in clay soil as it is in the scoria soil.

Intercalated water in clay may be released during milling resulting in a damp mixture less amenable to effective grinding.

Particle fracture may also play part in destruction of contaminants. Clays have a lamellar structure which, especially when wet, will cause some slipping when the clay particles are stressed thus reducing fracture.

The size of the initial particles may also be important. While this was not investigated, it is possible that if the soil particles are originally larger, there may be more fracture/size reduction and thus more potential for destruction such as are found in sandy soils with larger initial particle sizes.

The effect of soil type can also be seen from the results obtained from anthracene and phenanthrene destruction without addition of BHT. Anthracene destruction (section 3.6) results showed that the different soils have an effect on the destruction of anthracene. This can also be seen in table 4.5 below, which shows the concentration of anthracene remain in the soil after being milled for 120 minutes.

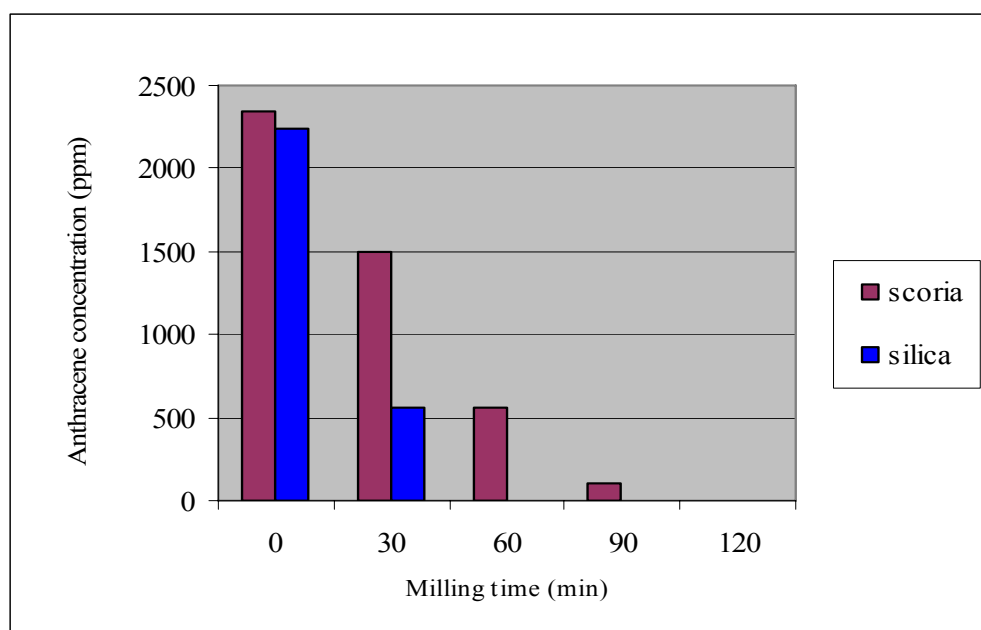


Figure 4.5: Comparison between scoria and silica sand milled at different time interval

From the above graph it can be seen clearly that the destruction efficiency is good in silica sand since anthracene was not detected from the sample milled for 60 minutes. All in all it can be concluded that the ball milling can be used to destroy anthracene because in both soil anthracene was not detected after being milled for 120 minutes.

The same trend of better destruction in silica sand was obtained in the phenanthrene destruction. Phenanthrene was not detected in the silica sand milled for 90 minutes, figure 4.6 below.

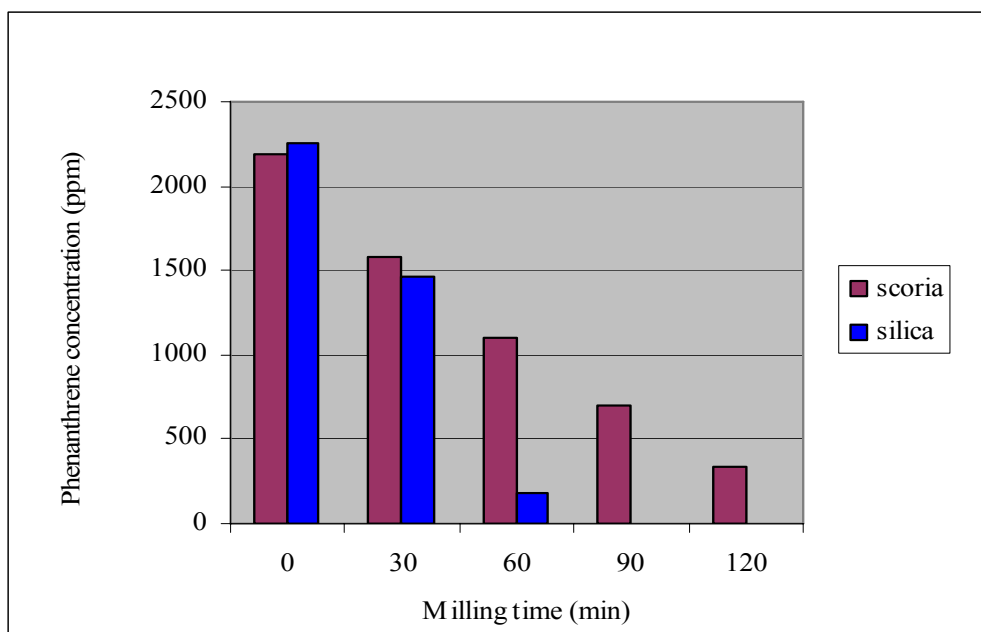


Figure 4.6: Comparison between scoria and silica sand milled at different time interval

Surprisingly there were no intermediates observed in the GC chromatograms of these experiments. This might be because of the difficulties in getting consistent results when stopping and starting the mill after very short periods of time, therefore 30 minutes was chosen as a minimum milling time.

Presumably smaller fragments are formed but these must have very short retention times on the GC. This indicates that once the contaminant undergoes an initial activation, the breakdown is rapid and extensive.

The results obtained for PAH destruction in different types of soil, showed that Ball milling can be used for the destruction of the three PAH's investigated. A similar trend is expected for other PAH's. Soil type had some effect on destruction efficiency. Silica sand was found to have the best destruction efficiency, followed by scoria and the clay soil.

The effects of varying moisture levels in the soil were not investigated but this is definitely something that should be investigated. As noted above, small amounts of

moisture may affect the milling process, the effect of larger amounts of water, or even wet milling is unknown.

4.1.3 Naphthalene destruction with and without addition of BHT

As it has been pointed out in chapter 2 section 2.4.3, BHT is a free radical scavenger, since it is assumed that the mechanochemical reaction that takes place during the milling process may be initiated by the formation of free radicals, the experiment of using BHT was done so as to determine if it may have any effect in the mechanochemical reaction (section 3.5). The results obtained were very good as can be seen clearly in figure 4.7. A low percentage destruction of naphthalene occurred when BHT was used compared to the same experiment conducted without BHT.

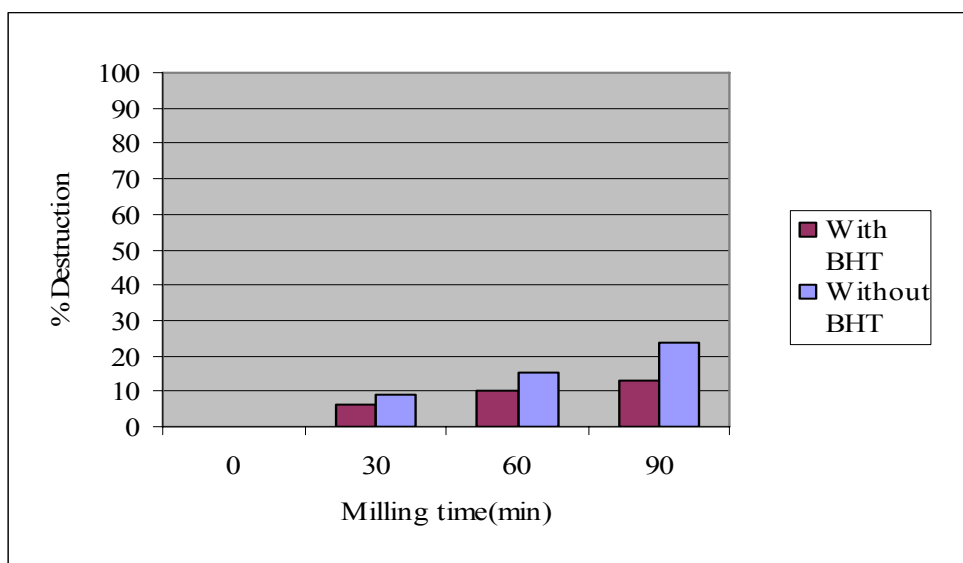


Figure 4.7: Comparison of naphthalene destruction in organic soil with and without BHT

However in the above graph the destruction efficiency of naphthalene without BHT was also very low compared to other naphthalene experiments. This is because in this experiment organic soil was used. The reduction of destruction efficiency on the addition of BHT was also seen from anthracene and phenanthrene. The graphs below show the effect of BHT in scoria and silica sand for anthracene and phenanthrene.

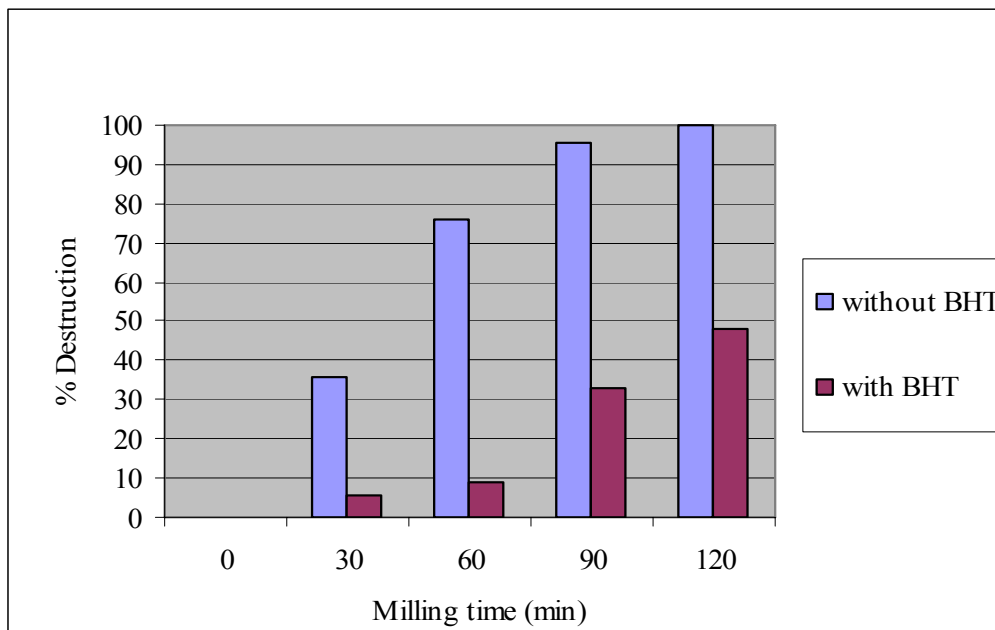


Figure 4.8: Comparison of anthracene destruction in scoria soil with and without BHT

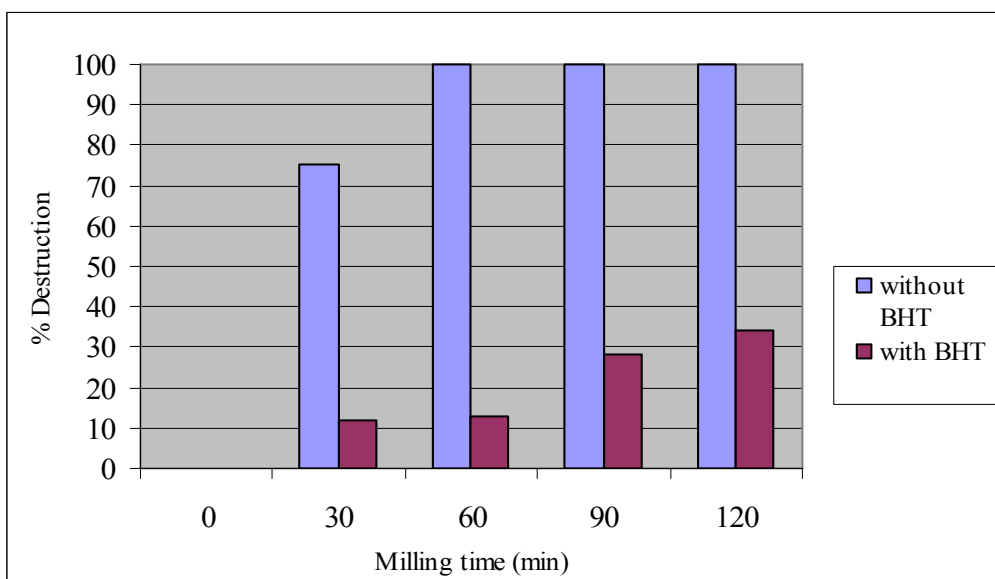


Figure 4.9: Comparison of anthracene destruction in silica sand with and without BHT

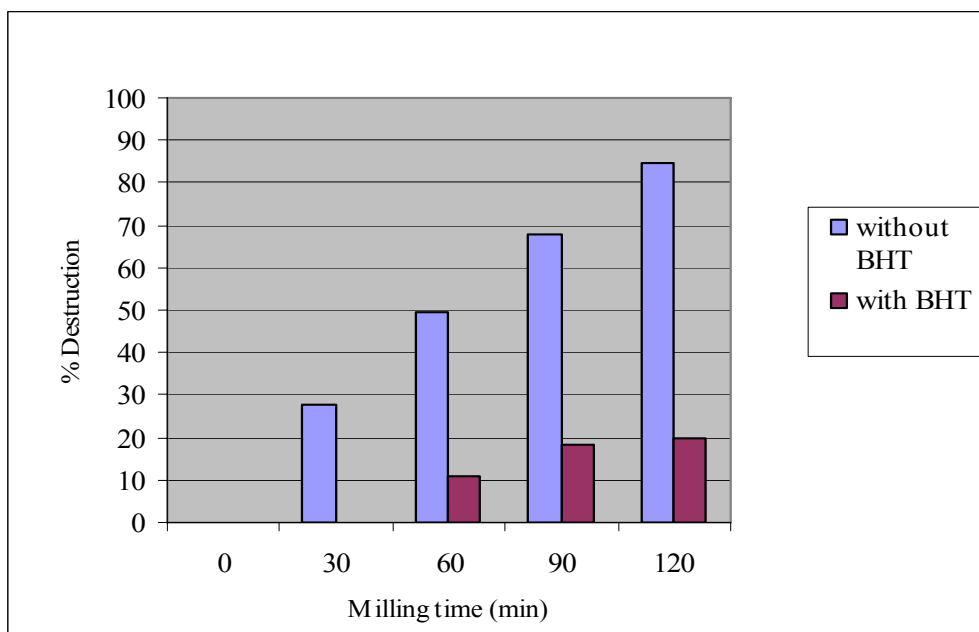


Figure 4.10: Comparison of phenanthrene destruction in scoria soil with and without BHT

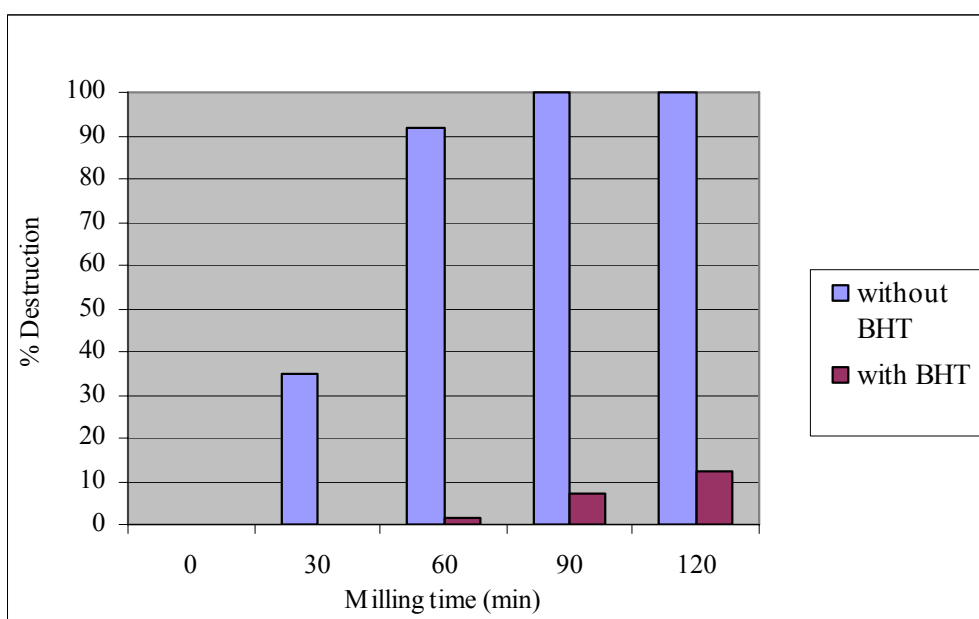


Figure 4.11: Comparison of phenanthrene destruction in silica sand soil with and without BHT

4.1.6 Phenanthrene destruction with addition of paraffin wax

Presence of paraffin wax in the soil was also investigated because during the milling of phenanthrene with BHT the treated soil had a greasy texture. The comparison of the effect of wax in the soil is as shown in figure 3.16 (chapter 3).

The results suggest that, the presence of any greasy substance in the soil has an effect on the mechanochemical destruction process. The drop in destruction efficiency may be due to a lubricating affect on the mechanochemical destruction process or the extra organic material is simply competing for the available energy. In all probability it is a combination of both effects.

4.1.7 Hydrocarbon destruction with and without addition of BHT

A similar experiment using BHT was conducted with the aliphatic hydrocarbons; n-eicosane and n-octacosane (chapter 3 section 3.6). It was also found that the BHT had a similar effect of decreasing the destruction rates of aliphatic hydrocarbons, figure 4.12 and 4.13.

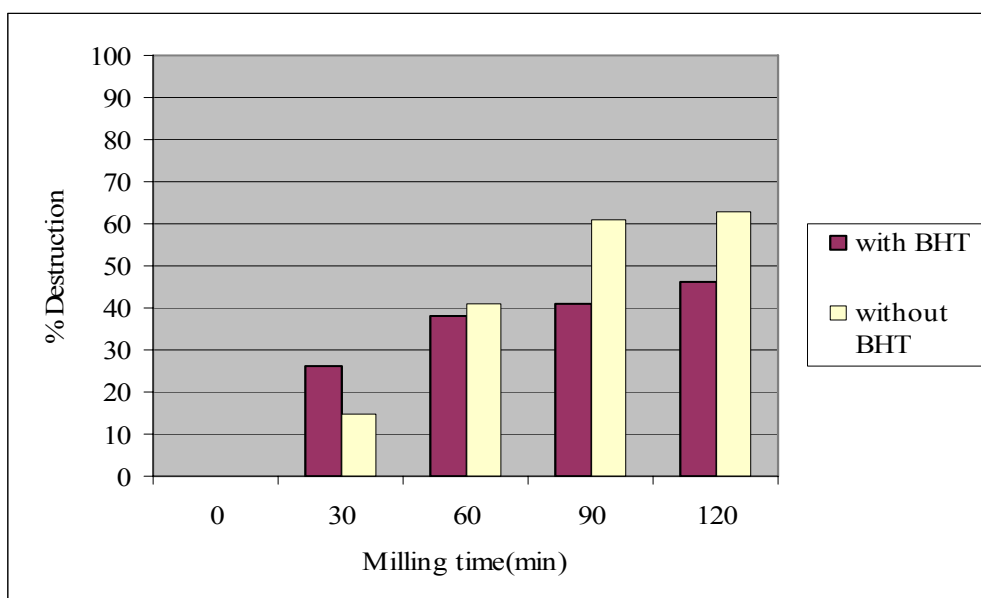


Figure 4.12: Comparison of destruction of n-eicosane with and without BHT

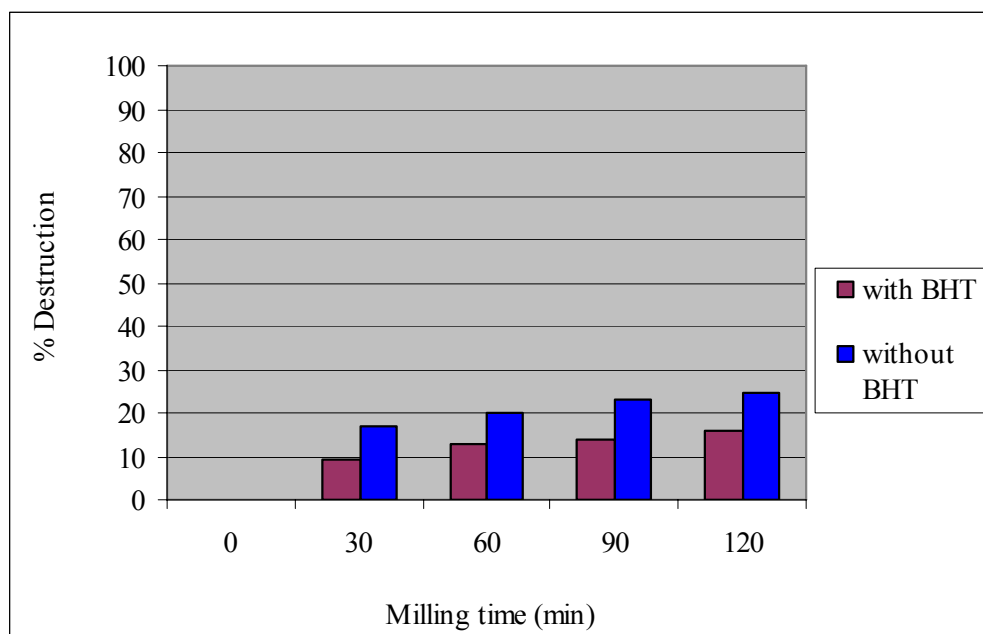


Figure 4.13: Comparison of destruction of n-octacosane with and without BHT

By comparing results obtained with the BHT experiments for both naphthalene and the aliphatic hydrocarbon, it can be seen that the presence of BHT significantly reduces the percentage destruction. Furthermore the unchanged BHT peaks were observed in the chromatogram, however for the naphthalene analysis in Chromatography BHT was taking long time to come out in the separation process of the GC-FID. But in the aliphatic hydrocarbon analysis BHT had a conveniently short retention time, its peak results was also recorded as presented in table 4.1.

Table 4.1: Milling of aliphatic hydrocarbons with BHT

Milling time	BHT	n-eicosane	n-octacosane
30	55445	3520	3950
60	57286	2930	3795
90	54164	2785	3765
120	55343	2560	3665

From the above table it shows that the BHT concentration was remained unchanged at the end of the reaction. So far from this project, the BHT mechanism in

mechanochemical reaction is for inhibition of the destruction efficiency is not clear. The BHT seems to be relatively stable in these mechanochemical reactions, this was a bit surprising but it was not further investigated.

4.1.8 Aliphatic hydrocarbon destruction with addition of Aluminium metal

There was no obvious trend in the results obtained with addition of aluminium metal. Comparing the results of n-eicosane milled with and without aluminium metal, table 3.22 and 3.26 in chapter 3, shows that the percentage destruction of n-eicosane was reduced by 10% due to the addition of aluminium metal while a comparison of table 3.24 and 3.27 for n-octacosane shows that destruction of n-octacosane with addition of aluminium metal was 2% higher than its destruction without aluminium metal.

The aluminium metal was added so that it could act as a catalytic substance due to its ability of forming metal surfaces during milling which can help in electrons transfer. But this was not observed.

4.1.9 Effect of sample volume in the milling

Table 3.24 (chapter 3) where 200 g of soil was used for milling, and table 3.28 (chapter 3) where 50 g of soil was used, showed that sample volume of soil contaminated with n-octacosane does not have much effect in the destruction process. The percent destruction obtained by milling 200 g of soil contaminated with n-octacosane for 120 minutes was 24% (table 3.24) while the percent destruction obtained after milling 50 g soil contaminated with n-octacosane for 120 minutes is 17% (table 3.28).

It was expected that the smaller sample volume used for milling would lead to much higher percentage destruction since there would be much room for the impacts and therefore better destruction will take place. However the results obtained did not show this. It might be due to the concentration of the contaminant, since the 50 g soil was highly contaminated nearly five times concentration of the contaminant as compared to

200 g. The low destruction efficiency obtained for 50 g soil used may also be due to the waxy, greasy nature of the soil with high n-octacosane contaminant.

4.1.10 Comparison between Destruction rate of hydrocarbons

The results from the hydrocarbons experiments were compared in tables 3.22, 3.23, 3.24, 3.25, 3.26, and 3.27 (chapter 3). They show that it is easier to destroy n-eicosane rather than n-octacosane, either with addition of BHT/Al or without.

It may be that the length of the carbon chain matters in the mechanochemical reaction. It may be possible that the longer the chain the more the energy is required for the reaction. However the C-C and C-H bonds are very unreactive due to their lack of significant polarity and the high bond energy. This needs to be further investigated.

4.1.11 Effect of milling time

Each experiment conducted in this project was done under different milling times; with the longer milling time used was 180 minutes. Time intervals were 30 minutes. From the results of all experiments, it is evident that the milling duration has a major effect on the destruction process by ball milling. This is similar to the results that Zhao (64) obtained. However, milling time should take into consideration of the percent destruction and the operating cost of the ball mill. The longer the milling time the higher the cost, therefore the destruction rate should be accounted relatively to the cost of the operation.

4.2 A SUMMARY OF PROPOSED MECHANISM OF BALL MILLING

There does not seem to be a good agreement among various authors on a theoretical basis of the reactive milling. There are two reasons for this:

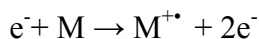
1. The goals of many researchers have been complete destruction rather than a careful examination of the mechanisms.
2. The chemistry is definitely “non-classical”. The environment in a running ball mill containing dry soil is not exactly any of the following:
 - A rarefied phase such as is found in molecular beam reactions
 - A gas phase
 - A solid phase
 - A homogeneous aqueous solution
 - A homogeneous non-aqueous solution
 - A heterogeneous aqueous solution/system
 - A heterogeneous non-aqueous solution/system

It is probably best described as a heterogeneous solid phase and gas phase mixture fluidised by the violent gas flows caused by the passage of the balls and subjected to repeated, highly localised, bursts of energy. Systems like this are not covered in typical text books.

In the destruction of organic compounds by ball milling, it is assumed that the destruction mechanism involves formation of free radicals from the contaminant. This is explained in the following sub sections:

4.2.1 Modes of Generation:

Assuming the "triboplasma" is real then free ions and electrons will exist momentarily at the point of impact. These can add or subtract electrons from molecules in much the same way as an electron impact source works for a mass spectrum.

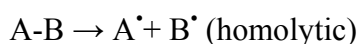
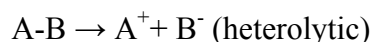


The resulting radical cation can decompose to give cations M^+ , radicals M^\bullet and neutral species M , there is transfer of energy as radical and/or radical ions.

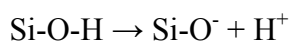
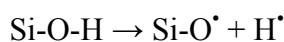
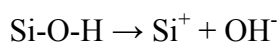
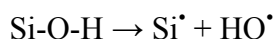
Other ions and species can of course be initially formed, M^- , and radicals etc.

4.2.2 Bond breaking.

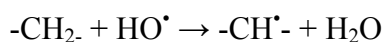
During the milling process chemical bonds can break to give ions or radicals. This can happen in two ways:



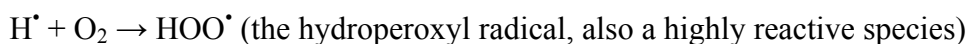
Both can be expected to give highly reactive species. Consider the Si-O-H bonds that are expected to be found on the surfaces of most silicate s. These could break to give e.g.



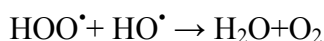
The hydroxyl radical in particular is a very reactive species that could be expected to combine, fairly indiscriminately with organic molecules. The hydroxyl radical has a significant involvement in the mechanisms of photochemical smog formation. Only one of its potential pathways would be to form other reactive organic radicals:



Many other mechanisms are possible, but the net result expected is that the principal mode of decomposition of organic molecules in the milling process is a multi pathway, free radical mechanism which results in a multitude of small fragments and products. Each is further subject to decomposition and ultimately leads to carbon and most probably H_2O .



One of a number of chain termination reactions would be



4.2.3 Cleavage of bonds

Any molecule with excessive energy it cannot transfer to its environment will break and/or rearrange its bonds. Examination of any text on mass spectrometry will show that there are thousands of ways a molecule can fragment. The results of the PAH's destruction in this study suggest that aromatic structures readily react. This is consistent with the stability of their ions in mass spectrometry.

It must be realised that the mass spectrometer has very dilute concentrations of ions in a high vacuum. In the conditions found in a mill, fragmentation will obviously be accompanied by reaction with other molecules, the surfaces in the system, oxygen, nitrogen, water and other gases (CO, CO₂ etc.) and other reactive molecules.

In some cases the products of such reactions can be seen.

It must not be forgotten that some molecules can cleave or rearrange at relatively low temperatures so some of the processes observed may be a result of a thermal decomposition or rearrangement. The initial dehydrochlorination of DDT to DDE (43) is an example of this. It is probable that most or all of this initial step occurs as a simple elimination.

4.2.4 Calculation of energy

The following calculation makes many assumptions but does give a result for the milling time consistent with observed milling times.

When a ball strikes a surface (the wall or another ball), by assuming that a 20 g (0.02kg) ball is travelling at 10m.s⁻¹ the energy ($\frac{1}{2}mv^2$) is 1 joule. And a C-H bond takes about 400 kJ.mol⁻¹ to break.

Assuming that a 20 g (0.02kg) ball is travelling at 10m.s⁻¹ the energy ($\frac{1}{2}mv^2$) is 1 J (joule). This localised cloud of energy is sufficient to break bonds. So long as

(presumably) the energy is high enough ($400 \div 6.02 \times 10^{23}$ kJ/C-H... very crudely for a C12 molecule this is 24 C-H bonds so each molecule needs $(400,000 \times 24 \div 6.02 \times 10^{23} = 1.6 \times 10^{-17}$ J). This then means that each impact could break 1.6×10^{17} molecules into C and H. about 0.3 μ mol. Assuming 30% efficiency this is ~ 100 nmol per ball impact. If we assume 50 impacts/second/ball. 20 balls is 1000 impacts/sec. If each impact is 1 joule this is 1000joules/sec. One hour of milling is 3,600,000 impacts or 3.6 kJ this is $(400/3.6)$, this 111 hrs/ mol of C-H 2667 or hours per mole of C12.

$$10^{-4} = 0.76 \text{ hours.}$$

It suggests that milling times should be in the order of 1 hour to 1000 ppm in 50 g of soil is 50mg of whatever. This is 3×10^{-4} mol of C12. $2667 \times 3 \times$ destroy a 1000 ppm C12 something. Remarkably close to what is observed.

As a summary, starting with PAH, it has been shown that the ball mill can be used as a mechanochemical reactor in the destruction of PAH's.

The results of aliphatic hydrocarbons showed that, the ball mill can be used for their destruction although more energy or time is required since the aliphatic hydrocarbons show low percentage destruction at times comparable to those which gave $\sim 100\%$ PAH's destruction.

CHAPTER 5

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The object of this study was to investigate the mechanochemical destruction of PAHs and aliphatic hydrocarbons using the ball milling process. Ball milling potentially uses low technology that can be made locally in places like Africa. It is simple to operate with relatively low operation cost and can be scaled from a laboratory scale to a large industrial scale. Ball milling remediation can be encountered without adding any other reactive substances to facilitate the reaction, and ball milling minimises the air pollution since it is a closed system, therefore there are minimal possibilities of toxic emission as compared to other methods of remediation such as incineration.

The investigation aimed at finding both the destruction efficiency using a variety of soil matrices and if possible to find the chemical mechanism for ball milling of PAH's and aliphatic hydrocarbons.

Naphthalene was chosen as the simplest PAH and a molecule which should give the fewest number of intermediates and products, other PAHs used were anthracene and phenanthrene. The aliphatic hydrocarbons chosen (n-eicosane and n-octacosane) were intended to be sufficiently large so that loss due to volatility would be reduced to minimum. And they would also be representative of compounds likely to be found after volatiles have evaporated from a hydrocarbon spill.

Experiments were carried out with different milling parameters which included different ball to soil ratios and different milling times. In some experiments BHT, Aluminium metal or parafin wax was added.

In this study, it has been found that operation parameters such as ball to soil ratios, milling time, soil type and the contaminant properties, affect rates and extents of pollutant removal. It was found that the higher number of balls the higher the percent destruction obtained. The longer the milling time, the higher the destruction efficiency obtained. Though during the destruction process the milling time should be optimized so as to have reasonable operation cost.

It was also found that, each type of contaminant behaved differently in the mechanochemical process, by comparing the results of all the contaminants used. PAHs (naphthalene, anthracene and phenanthrene) were the easiest to be destroyed compared to aliphatic hydrocarbons (n-eicosane and n-octacosane). The ball milling works really well for the PAH's investigated and probably it will work for other PAH's due to their similarities in their chemical structures.

Aliphatic hydrocarbons are also destroyed, just more slowly. High energy ball mill with more milling duration will increase the destruction rate.

Surprisingly there were no intermediate products observed for all contaminants investigated. It was expected for aliphatic hydrocarbons the breakage of the chain may occurred and forming different short chains, for example starting with hydrocarbon with C28 and obtained C25, C20 or other short chains. This was not observed.

Addition of the BHT to the mechanochemical reaction reduced the percentage destruction for all contaminants used. Also addition of paraffin wax reduces the destruction efficiency to all contaminants investigated. It was found that, presence of lubricants such as wax in the contaminated soil appeared to inhibit the mechanochemical reaction.

Since it is practicably impossible to have zero contamination in our environment, the proper way of environmental remediation required. As far as the investigation of ball milling is concerned in this study, ball mill can be regarded as one of the efficient method for the environmental remediation.

5.2 RECOMMENDATION

This study shows that the ball milling can be used for the destruction of PAH's and aliphatic hydrocarbons. The results for aliphatic hydrocarbons showed that they will be more difficult to destroy than aromatic hydrocarbons under the same conditions.

More experiments are needed to investigate the ability of ball mill to destroy branched hydrocarbons and alkyl aromatics. Also research is need for the soil contaminated with mixtures of aromatic and aliphatic hydrocarbons to see if they have any synergistic relation.

As it was observed that presence of moisture example in clay soil may have effect on the mechanochemical reaction, there is a need to investigate the mechanochemical process in wet milling. Since soils will have highly variable moisture contents.

Also the effect of lubrication in the mechanochemical process was not very clear, as it is assumed that there might be a competition of the lubricant substance with the contaminant to the energy required for the destruction or there is reduction of milling effectiveness which leads low destruction. More research should be done with different types of lubricants.

The effects of other antioxidants needs to be investigated as BHT was found to be relatively stable in the mechanochemical reactions.

The following are factors which may affect the milling process and they are needed to be studied prior to the milling process.

- i. Soil composition and characteristics
- ii. Properties of the contaminant
- iii. Optimum milling duration
- iv. Ball to soil ratio

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