The Effect of Soil type, Water and Organic Materials on the Mechanochemical Destruction of Organic Compounds

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ATTESTATION OF AUTHORSHIP

"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 (except where explicitly defined in the acknowledgements), nor material which to a substantial extent has been submitted for the award of any other degree or diploma of a university or other institution of higher learning."

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ABSTRACT

Persistent organic pollutants are a well-known threat to the environment. Substances such as polycyclic aromatic hydrocarbons and chlorinated compounds have severely detrimental effects on health for both humans and animals. These toxic organic substances are mainly introduced into soils and groundwater by pesticide use and industrials by products.

There is a dire need to develop soil remediation techniques that are efficient, cost effect and relatively uncomplicated. The need is especially great for developing countries that have an obsolete pesticide stockpiles problem.

Mechanochemical remediation is an ideal candidate to fill that need. Mechanochemical activation by ball milling was originally developed for mineral processing. It has proved to be an extremely versatile technique and was found to be able to degrade toxic organic compounds.

In this study reactive ball milling was used to investigate the destruction rates of naphthalene, chloronaphthalene and diesel in different kinds of soil. Naphthalene, chloronaphthalene and diesel were used as organic pollutant analogues. A GC-MS was used to analyse and quantify the destruction rates. It has been suggested that Total Organic Content (TOC) analysers can also be used to analyse the destruction rates, but a TOC analyser was not available. Quartz had the highest overall destruction rate followed by scoria, limestone, subsoil, greywacke, china clay and terracotta clay.

In past studies, it was found that water would hinder destruction efficiencies but no reason as to why or how water did this. This study also looked at why water was reducing destructive capacities of the soils. Water was reacting with the

radicals generated by the milling therefore decreasing the total radical available that would react with the target pollutants.

The study also looked the effects of organic matter has on the destruction rates of naphthalene. Cellulose powder was added to the sample soils and it was determined that it also decreased the destructive capacities of the soil. The cellulose was sequestering the naphthalene initially, but with continued milling the cellulose and naphthalene were degraded.

The effects of ball milling on soil health were also studied. Soil structure and aggregation were altered, but tillage of the milled soil and mixing it with unmilled soil would create healthy aggregation and the sample soils tested were all able to sustain plant life. The study also looked how soil bacteria would react to ball milling. It was determined that the bacteria did not survive the milling process, but milled soils were successfully inoculated by bacteria.

Chapter 1 - Introduction

The aim of this study was to better understand the mechanism of the mechanochemical destruction (MCD) of organic pesticides, polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs). It is important to better understand the sequence of events that occur during the mechanochemical destruction of contaminants in a sample of soil in order to maximise the destructive efficiency. If a set of parameters is found that maximises the destructive capacity of the MCD technology, future remediation of soil contaminated by pesticides, PAHs and POPs would be done more efficiently, cheaper and shorten the remediation time.

Past studies have suggested that the MCD technology works and is a real decontamination option. However, there are a few issues that have still not been studied. Some of these issues are the effect of water and soil type on the MCD efficiency. Water is known to reduce the destruction efficiency of the MCD technology but the exact effect of water on the breakdown mechanisms have not be studied and still remains to be answered. Furthermore, there is no set guideline for contaminate half-lives versus soil type within a mechanochemical decontamination context. Therefore, part of this study will try to create a contaminant half-life guideline for different soil types.

The study will also look into the effect the MCD technology has on the microbiology of the soil and whether it affects soil fertility.

1.1 New Zealand Industry and Pollution

Soil contamination is caused by the presence of xenobiotic chemicals or other alteration in the natural soil environment. This type of contamination typically arises from the rupture of underground storage tanks, application of pesticides, and percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, and heavy metals. This occurrence of this phenomenon is correlated with the degree of industrialisations and intensities of chemical usage.

The concern over soil contamination stems primarily from health risks, from direct contact with the contaminated soil, vapours from the contaminants, and from secondary contamination of water supplies within and underlying the soil. Mapping of contaminated soil sites and the resulting clean-up are time consuming and expensive tasks, requiring extensive amounts of geology, hydrology, chemistry and computer modelling skills.

Soil is a sort of ecosystem unto itself, and it is relatively sensitive to foreign matter being applied to it. That is good in the case of wanting to add soil amendments, fertiliser and compost to make the soil healthier, but not so good when it comes to soil pollution.

New Zealand has had its share of encounters with chemical pollution; from pesticides and fertilisers to preservatives and hydrocarbons. Most of the contaminants in New Zealand are attributed to pesticide use. As New Zealand relies heavily on its agricultural industry, a lot of pesticides were used in the

past to maximise profits. New Zealand cultivates a wide variety of agricultural exports like fruits, grains, vegetables, seeds, bulbs and flowers. New Zealand's signature fruit export is the Kiwifruit; there are over 2700 kiwifruit growers with over 13000 hectares planted (New Zealand Official Yearbook 2008). In 2006, over 80 million trays were exported which equates to over 25% of the world's kiwifruit production. Other fruits that are exported are citrus fruits, avocados, blackcurrants, other berries and grapes. At the end of the 2007 financial year, New Zealand had exported NZD$1,200 million of fresh fruits, NZD$105 million of processed fruit and NZD$698 million of wine (which equates to 76 million litres of wine) (New Zealand Official Yearbook 2008). New Zealand also exports a wide variety of vegetables; 50 different vegetables are estimated to be grown here. Approximately 50,000 hectares of land is dedicated to the cultivation of vegetables and about 1,450 commercial growers tend to the land. In 2007, New Zealand exported NZD$400 million worth of fresh and frozen vegetables. The seeds, bulbs and flower market are also an important agricultural product for New Zealand. Approximately NZD$60 million worth of seeds and bulbs were exported and approximately NZD$40 million worth of flowers and foliage was exported in 2007 (New Zealand Official Yearbook 2008).

It is quite evident that New Zealand has a thriving agricultural based industry which also provides jobs for thousands of New Zealand workers. It is therefore imperative to sustainably manage and use the huge areas of farm and agricultural land to maintain the cultivation of the aforementioned products. Part of this sustainable management is the acknowledgment that the proper use of pesticides, herbicides and fungicides is an important aspect of the industry. In the past, New Zealand used some of the pesticides that are now known to be hazardous to both the environment and people. Some of the main pesticides

that were used are 2,4,5-trichlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, bromomethane, DDT, DDD, dieldrin, polychlorinated biphenyls, lindane, aldrin, hexachlorobenzene, heptachlor and endosulfan. All these pesticides have been deemed toxic and have since been banned.

Another industry which directly impacts land and is a potential avenue of land pollution is pastoral farming, namely, dairying and livestock. The New Zealand meat industry is as important as the export of agricultural products, it is the second largest food export worth NZD$5.14 billion in 2009. That is approximately 13% of New Zealand's total exports.

New Zealand is the eighth largest producer of milk, with about 2.2% world production. Total production was 1.3 billion kg of milk solids, and NZD$8.38 billion of dairy products were exported in the year ending 30 September 2007 (New Zealand Official Yearbook 2008). Both the livestock and dairying industries rely on land to rear and sustain the livestock.

Another environmental problem relating to the rearing of livestock is the use of sheep dips and foot baths. Sheep dips are used to protect sheep from infestation against external parasites and foot baths were used to prevent footrot. This is achieved by "dipping" the sheep in a liquid formulation of pesticide, fungicide and toxic elements. Sheep dips and foot baths have been used in New Zealand since the 1850's and it was even made compulsory by various Acts of Parliament between 1908 and 1993 (ECAN 2003).

Up until the 1950s, the toxic metalloid arsenic was mainly used in both sheep dips and foot baths but its use was phased out due to its toxic effects. After the arsenic phase out, farmers turned to organochlorine and organophosphate pesticides like DDT, dieldrin, Lindane and diazinon (ECAN 2003) until their toxic

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effects were revealed. More recently synthetic pyrethroids and insect growth regulators (IGRs) have been, and still in use. These new insecticide, though less toxic than organochlorines and phosphates, are still harmful is released in the environment at high levels. According to an article published in 2008, there seems to be a correlation between pyrethrins and autism (Hertz-Picciotto 2008). In the study of 500 children (with or without autism), the 138 children with autism and their mothers were twice as likely to "report using pet shampoos and other household products containing pyrenthrins than other mothers". Further investigation into the causal link is still being carried out (Hertz-Picciotto 2008).

The current best estimate is that there are around 50,000 sheep dips across New Zealand (EW 2006). This huge number of contaminated sites greatly increases the chances of exposure to human both directly or indirectly. Abandoned sheep dips also threaten our meat exports as livestock can be unknowingly feeding on pastures grown over old sheep dip sites. There was a case in Australia that reports a large shipment of meat exports were refused entry into the United States in 1987 due to the meat having high traces of organochlorines.

Like the agricultural industry, the side effects of rearing huge numbers of farm animals are evident in the land used to farm these animals. The use of fertilisers, sheep dips and the introduction of manure and urine are directly harmful to the soil and surrounding environment e.g. effluent discharge into streams and rivers.

It is in New Zealand's best interest to keep the land healthy and contamination free. This can be achieved by sustainably managing the land and following the guidelines set out by the various regional councils and by the remediating

existing contaminated sites by techniques which are safe, effective and relatively cheap.

Another industry that has used chemicals is the timber industry. They used fungicides to protect freshly sawn timber to protect them various types of fungal growth. The use of some of these fungicides has been banned as they have now been discovered to cause serious health problems to people exposed to them. These fungicides also tend to remain unaltered in the environment and therefore many of the timber mills around the country are considered contaminated sites.

Keeping New Zealand's land healthy is vital for its future, 17% of New Zealand's GDP depends on the top 15 cm of its soil and failure to sustain the soil and water resources will put $2.16 billion of the total GDP at risk.
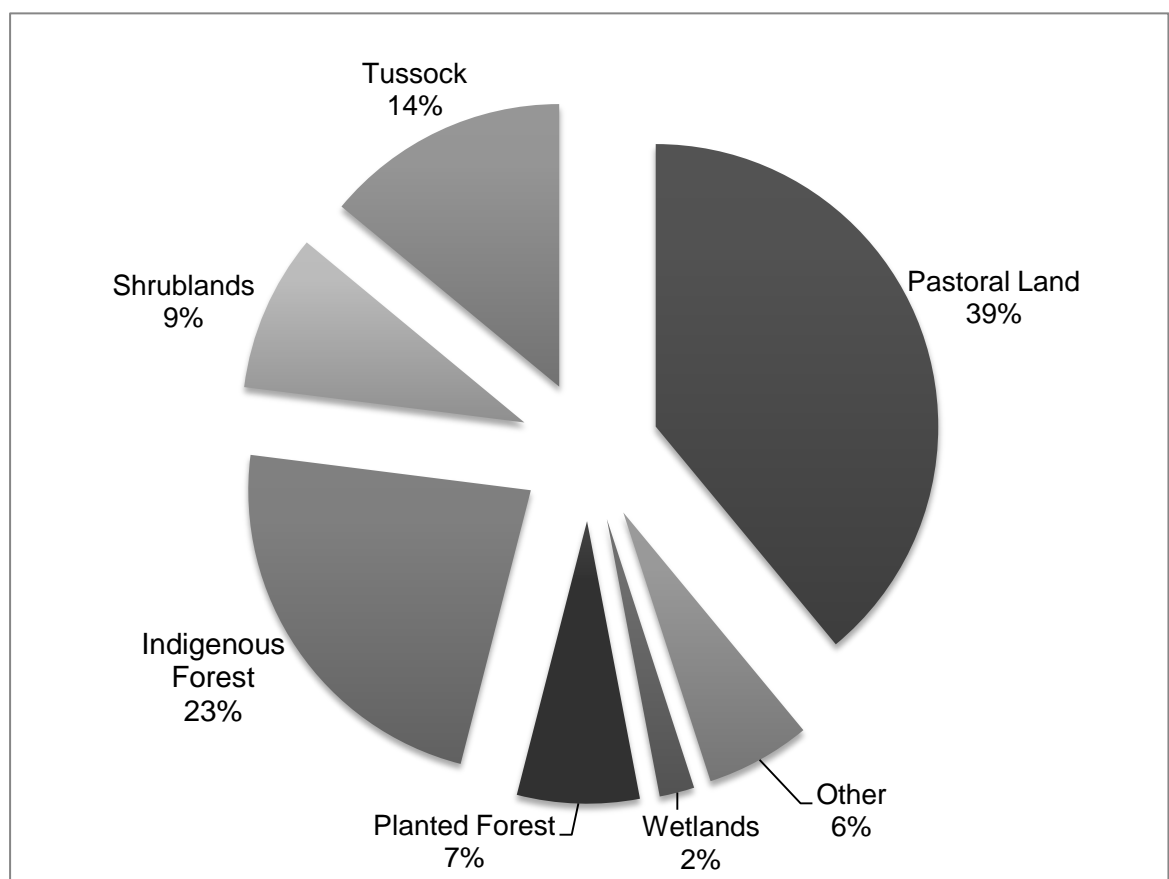
Figure 1.1 – Land use in New Zealand

1.2 Banned Substances

There are many naturally occurring and synthetic substances that have been recognised for their toxic effects and have been banned from use.

Many countries have made is illegal to use, manufacture and import toxic chemical substances like the United States and the countries of the European Union. Furthermore, there are global organisations like UN and WHO that have drafted environmental treaties that ban toxic substances.

Within the context of land contamination, herbicides, insecticides, fungicides and by-products of industry pose the threat. The agricultural industry has been exponentially growing since in the late 1930s due to the discovery of pesticides. They have protected crops and allowed for high profitable turnover, however, many of these pesticides turned out to be severely toxic to humans and the environment.

The main chemicals that pose a threat and persist in the environment, especially in soil and groundwater are informally known as "The Dirty Dozen":

Table 1.1 - Dirty Dozen

Aldrin	Chlordane	DDT
Dieldrin	Dioxins	Endrin
Furans	Heptachlor	Hexachlorobenzene
Mirex	PCBs	Toxaphene

The Dirty Dozen are all persistent organic pollutants (POPs), they are all toxic to humans and as the name suggests, persist in the environment without

degrading and can bioaccumulate. In 1995, the governing council of the United Nations Environment Programme (UNEP) called for global action to be taken on POPs. The Intergovernmental Forum on Chemical Safety (IFCS) and the International Programme on Chemical Safety (IPCS) were tasked to prepare an assessment of the worst offenders, which now are known as the "dirty dozen".

The negotiations for the Stockholm Convention were completed on 23 May 2001 in Stockholm, Sweden. The convention entered into force on 17 May 2004 with ratification by an initial 128 parties and 151 signatories. Co-signatories agree to outlaw nine of the dirty dozen chemicals, limit the use of DDT to malaria control, and curtail inadvertent production of dioxins and furans.

Parties to the convention have agreed to a process by which persistent toxic compounds can be reviewed and added to the convention, if they meet certain criteria for persistence.

During the fourth review meeting held from 4 to 8 May 2009, the Conference of the Parties, by decisions SC-4/10 to SC-4/18, adopted amendments to Annexes A (elimination), B (restriction) and C (unintentional production) of the Stockholm Convention to list nine new chemicals as persistent organic pollutants:

Table 1.2 - The nine new POPs

Alpha hexachlorocyclohexane	Beta hexachlorocyclohexane	Chlordecone
Hexabromobiphenyl	Hexa and heptabromodiphenyl ether	Lindane
Pentachlorobenzene	Perfluorooctane sulfonic acid and perfluorooctane sulfonyl fluoride	Tetra and pentabromodiphenyl ether

1.3 Common Pollutants in New Zealand and the World

As mentioned in the earlier section, New Zealand has used a wide variety of pesticides, herbicides and fungicides to maximise the agricultural, timber and dairy/livestock outputs. Some of these chemicals have since been banned due to their toxic nature; however residues of these chemicals can still be found on produce and in the land and many of them are still being used today in developing countries.

Some of these pesticides, herbicides and fungicides are listed and discussed below.

1.3.1 Pentachlorophenol
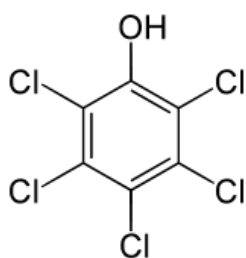
Pentachlorophenol (PCP) is a persistent organochlorine compound. It is a white organic solid with needle-like crystals and a phenolic odour (WHSQ 2010). PCP was introduced into the environment through its use as a pesticide, herbicide, insecticide and a timber preservative (ERMA 2005).

Pentachlorophenol is used as an industrial wood preservative for utility poles, crossarms, fence posts, as well in mill uses, consumer wood preserving formulations and herbicide intermediate (Choudhury 1986). As a wood preservative, pentachlorophenol acts as both a fungicide and insecticide (Choudhury 1986). The mill uses primarily involve the application of pentachlorophenol as a slime reducer in paper and pulp milling and may constitute ~6% of the total annual consumption of pentachlorophenol (Choudhury 1986). Sodium pentachlorophenate (NaPCP) is also used as an

antifungal and antibacterial agent (Choudhury 1986). Pentachlorophenol also is used as a general herbicide (Choudhury 1986).

PCP is synthesised by the chlorination of phenol in the presence of either aluminium or ferric chloride which acts as a catalyst at a temperature around 191°C (Yu 2004). This process does not result in complete chlorination and commercial PCP is only 80-90% pure. Unfortunately, some of the products or contaminants created during the process are more toxic than PCP. Some of these contaminants are polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Yu 2004).

Pentachlorophenol was used in New Zealand as a fungicide in the timber industry from the 1950's through to the late 1980's. For most of this period, virtually all freshly sawn timber produced in the country, predominantly radiata pine was routinely surface treated to prevent the proliferation of sapstain fungi. The most commonly used process involved dipping the timber in baths containing an aqueous solution of the sodium salt of PCP (NaPCP). In addition, pressure treatment with a PCP in oil mixture was used as an alternative preservative treatment to creosote (Davenhill 1995).

Exposure to PCP can occur through the work place of by the general environment. People working in the wood preservative industries have a high chance of being exposed to PCP. They can be exposed to PCP via dermal contact or via inhalation. The general public can also be at risk of exposure by the inhalation of contaminated air, ingestion of contaminated ground water used as a source of drinking water, ingestion of contaminated food, and dermal contact with soils or products treated with the chemical (ATSDR 1999).

Livestock exposure to large amount of PCP can have deleterious effects on the liver, blood, lungs, kidneys, nervous, digestive, endocrine, and immune systems

(Beard 1999). Contact with PCP in vapour form can irritate the eyes, skin and mucosal membranes and is also classified as probable human carcinogen by the U.S Environmental Protection Agency.

1.3.2 Dichlorodiphenyltrichloroethane (DDT)
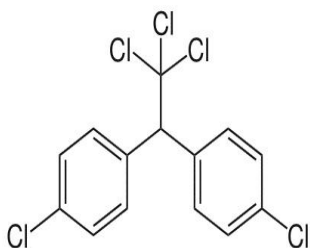
Dichlorodiphenyltrichloroethane is also a persistent organochlorine compound. It is extremely hydrophobic and has a crystalline structure. It is colourless, has a weak odour and is nearly completely insoluble in water, but is soluble in most organic solvents, oils and fats. DDT is not a naturally occurring molecule, it is produced by reacting chlorobenzene with chloral and the reaction is catalysed by sulphuric acid. DDT was first synthesised in 1874, but its properties as a pesticide were discovered in 1939. It was initially used to control malaria and typhus among troops and civilian populations during the second half of World War II. After the end of the war, it was produced in vast quantities as a pesticide from 1950 to 1980 (Geisz 2008). There has been some concern on DDT's negative environmental and biological impacts reported by scientists as early as the 1940s, but their concern received little attention. In the late 1950s, naturalist author Rachel Carson came across an article in The New York Times which highlighted the unsuccessful attempts to restrict DDT use. She then started to write a piece on the subject which evolved into a book titled *Silent Spring* which was published in 1962; the book garnered a huge readership and quickly became a best seller. It argued that pesticides, including DDT, had adverse effects on the environment, ecology and people. It is also accepted that the book sparked the environmental (green) movement. DDT was also extensively used here in New Zealand in the 1950s and 1960s; as

much as 500 tonnes was being applied annually (Salmon 1959). It was used to control the Porina Moth and the Grass Grub and was also applied on lawns. New Zealand followed the global trend of DDT restriction in the 1970s and was finally banned in 1989 (Taylor 1997). In 2001, The Stockholm Convention on Persistent Organic Pollutants (DDT included), was signed in an effort to eliminate and/or restrict production and use of persistent organic pollutants. The treaty was officially passed and took effect in May 2004.

DDT has adverse effects on both the environment and on human health. DDT was first to be intended to be used as pesticide, but it was a none-selective pesticide. It did not just attack the target pests and insects; it also had adverse effects on mammals, marine and bird life. The most famous effect it had was its action as a reproductive toxicant for certain bird species. DDT would interfere with the blood-calcium levels and cause it to decline. This would decrease the amount of calcium available for eggshell development; therefore eggs with very thin and brittle shells are laid. The weakened eggs usually break during the incubation time and this leads to decreases in avian populations. Some of the avian species affected by eggshell thinning are the Osprey, the Bald Eagle, the Brown Falcon and the Peregrine Falcon (ATSDR 2002; Stokstad 2007; DOI 2008).

Humans are also affected by DDT with potential mechanisms of actions via endocrine disruptions and genotoxicity. It has been reported by various studies that Human DDT exposure can cause developmental and reproductive toxicity e.g. decreases in semen quality, menstruation, length of gestation and lactation (Cohn 2003; Rogan 2005; De Jager 2006; Aneck-Hahn 2007; Nagayama 2007; Jurewicz 2009). It is also known to be a carcinogen as there is evidence from epidemiological studies that indicate that DDT causes cancer of the liver,

pancreas, and breast (Rogan 2005; Eskenazi 2009). There is mixed evidence that it contributes to lymphoma, leukemia and testicular cancer (Rogan 2005; Spinelli 2007; McGlynn 2008; Eskenazi 2009).

1.3.3 2,4-Dichlorophenoxyacetic acid (2,4-D)
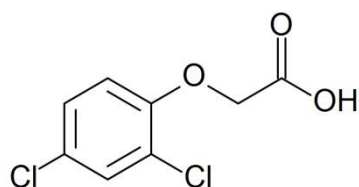
2,4-Dichlorophenoxyacetic acid or 2,4-D is another persistent organic pollutant that was used as a pesticide/herbicide. 2,4-D is not banned by an environmental treaty and is the most widely used herbicide in the world (Ibrahim 1991).

Being a synthetic auxin (plant hormone), its mechanism of action is to translocate to the plant's meristem which results in uncontrolled and unsustainable growth. This will cause leaf stem curl-over, withering and eventual death.

2,4-D does not occur naturally on the environment. It is manufactured by reacting 2,4-dichlorophenol and chloroacetic acid, however the reaction also produces unwanted impurities which are far more toxic than 2,4-D (IPCS 1994; WHO 1989).

It was first synthesised in the United States in 1942 and has been manufactured in New Zealand from 1962 until December 1988 (Dow-Elanco 1993).

One of the impurities produced of most concern are dioxins (WHO 1989). Tetrachlorodibenzo-p-dioxin (TCDD) is classified as a human carcinogen by the International Agency for Research on Cancer (Eriksson 1981), however the contamination of the 2,4-D usually occurs by similar molecules to TCDD but with varying amounts of chlorine (sometimes with 2 or 3 chlorines instead of 4). In 1977, Eriksson et al. saw several patients with soft-tissue sarcomas and

previous exposure to phenoxy acids. This clinical observation resulted in a cases-referent (case-control) study being undertaken which showed that exposure to phenoxy acids or chlorophenols, which are chemically related, gave a roughly six-fold increase in the risk for this type of tumour. A further case-referent study of soft-tissue sarcomas has now been performed to confirm these earlier findings and also to obtain further information on the effects of different phenoxy acids. This new investigation gave an increase of the same magnitude in the risk for soft-tissue sarcomas after exposure to phenoxy acids or chlorophenols, but this risk related also to exposure to phenoxy acids free from impurities, such as polychlorinated dibenzodioxins and dibenzofurans.

2,4-D is still in use today in New Zealand and it has possibly caused millions of dollars' worth of damage to vineyards in Hawkes Bay (AgroNews 2010). 2,4-D is known for its damaging drift and is highly hazardous to sensitive plants like grapes.

1.3.4 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
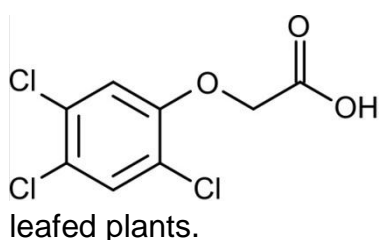
2,4,5-T is very similar to the 2,4-D. 2,4,5-T is also a synthetic auxin and is a chlorophenoxyl acetic acid. It is also used as a herbicide to defoliate broad-leafed plants.

Both herbicides were developed in the late 1940s but was phased out by the 1970s as concern grew from its toxicity and the terrible affects it had on the people if Vietnam when it used as one of the ingredients in Agent Orange (the other ingredient being 2,4-D), however the main cause of the adverse effects were caused by the contaminant TCDD (Eriksson 1981).

In 1985, the United Stated Environmental Protection Agency banned the use of 2,4,5-T and as part of the Rotterdam Convention was signed by 73 signatories, the international trade of 2,4,5-T has been restricted.

1.3.5 Endosulfan
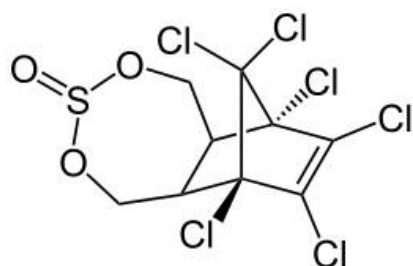
Endosulfan is an organochlorine based insecticide. It was developed in the early 1950s and by the 1980s, it was estimated that world-wide production of endosulan was around 9,000 metric tonnes (WHO 1984) and the production has increased to around 13,000 metric tonnes in the 1990s.

The synthesis of endosulfan is dependent on the Diels-Alder reaction of hexachlorocyclopentadiene with cis-butene-1,4-diol and subsequent reaction of the adduct with thionyl chloride (Signorella 1993). Endosulfan is still in use today and is considered the most toxic insecticide on the market today. Many countries have taken the initiative to ban the use and manufacture of endosulfan within their borders. Some of the countries that have already banned endosulfan are the United States, Australia, New Zealand and the European Union. In New Zealand, the Environmental Risk Management Authority (ERMA) banned endosulfan manufacture, import and use in 2009. Due to the toxic threat endosulfan poses to human health; a global band has been implemented under the Stockholm Convention in April 2010 which will take effect in mid-2012.

Even with the adverse effects endosulfan has on both humans and the environment, many countries are still manufacturing and using it, predominantly China and India. Both countries and other smaller nations that are still using

endosulfan have reported thousands of cases of injury and death due to acute endosulfan exposure (van der Hoek 2006).

When endosulfan is released into the environment, it breaks down into endosulfan sulfate and endosulfan diol, both of which, according to the EPA have "structures similar to the parent compound and are also of toxicological concern (USEPA 2002).

The estimated half-lives for the combined toxic residues (endosulfan plus endosulfan sulfate) range from roughly 9 months to 6 years." The EPA concluded that, "based on environmental fate laboratory studies, terrestrial field dissipation studies, available models, monitoring studies, and published literature, it can be concluded that endosulfan is a very persistent chemical which may stay in the environment for lengthy periods of time, particularly in acid media." (USEPA 2002)

The EPA also concluded that "endosulfan has relatively high potential to bioaccumulate in fish." (USEPA 2002) The US Environmental Protection Agency has classified endosulfan as "Category I: Highly Acutely Toxic" based on the LD_{50} value of 30 mg/kg for rats (USEPA 2002). According to the Agency for Toxic Substances and Disease Registry (ATSDR 2002), endosulfan mechanism of action in mammals including humans is a GABA-gated chloride channel antagonist and a calcium and magnesium ion ATPase inhibitor (ATSDR 2000). This mechanism of action gives endosulfan its neurotoxicity.

1.3.6 Hydrocarbon Fuels

In today's industrialised world, instances of industrial areas contaminated by petroleum hydrocarbons are numerous. One of the main derivatives of petroleum is diesel. The product is thought to be named after Dr Rudolf Diesel, a German engineer who, in 1892, patented an oil-burning internal combustion engine. Diesel is a complex mixture of saturated (60–80% of n-alkanes and naphthenes) and aromatic hydrocarbons (20–40%) (Khalladi 2009; Falciglia 2011)

It is one of the most commonly used fuels today therefore poses a huge risk in terms of environmental contamination. Diesel is used to power most industrial machinery like trucks, ships, factories, military vehicles, farm machinery and many other combustion engines. Due to its heavy use, the chances of accidental exposure of diesel to the environment also increase.

Under normal industrial or domestic use, dermal contamination is the most likely exposure scenario. Chronic or repeat human exposure to diesel may result in dermatitis although there is some evidence to suggest that hyperkeratosis may be a common feature of regular contact with diesel (IPCS 1996). Land with high concentration diesel contamination poses a risk due to it being readily vaporised. Reidenberg et al. reported a case a lorry driver was exposed to (an unknown concentration of) diesel vapour over a ten day period. Signs and symptoms included abdominal cramps, nausea, vomiting, acute renal failure, anaemia and thrombocytopenia (Reidenberg 1964).

Hydrocarbon fossil fuels also have detrimental effects on plant life. Walker et al. studied the effects of crude and diesel oil spills on plant communities at

Prudhoe Bay, Alaska by spilling diesel and crude oil on six of the major Prudhoe Bay plant communities at an intensity of 12 litres/m^2 (Walker 1978). The communities occurred along a topographic-moisture gradient. The reaction of the major species of the various communities was recorded one year following the spills.

Sedges and willows showed substantial recovery from crude oil spills. Mosses, lichens, and most dicotyledons showed little or no recovery. On a very wet plot with standing water, the vegetation showed total recovery one year following the spill (Walker 1978).

Dry plots, on the other hand, showed very poor recovery. *Dryas integrifolia* M. Vahl, the most important vascular species on dry sites, was killed. Identical experiments using diesel oil rather than crude oil showed all species except an aquatic moss to be killed (Walker 1978).

The studies demonstrate that diesel and crude oil spills are both hazardous to animal and plant life, in both dry and wet conditions.

1.4 Obsolete Pesticides

The agricultural industry has been exponentially growing since in the late 1930s due to the discovery of pesticides. Namely, DDT was discovered to have insecticidal properties which allowed for crops to grow unhindered which allowed for the agricultural industry boom.

Ever since that day the agrichemical industry has been producing tonnes of different types of pesticides per year and have recorded yearly revenues in the tens of billions of dollars (FAO 2000).

The International Code of Conduct on the Distribution and Use of Pesticides defines pesticides as:

"Any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant, or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport" (FAO 1990).

An estimated 25 million people per year are poisoned by pesticides (Davis 2002) and from those; approximately 20,000 of them are killed (WWF 1997). The vast majority of pesticide poisoning victims are from the developing countries. This disparity is due to the stockpiling of huge amounts obsolete pesticides; the FAO Obsolete Pesticide Program reported that up to 500,000 tonnes of obsolete pesticides are stockpiled in the developing countries.

One of the factors that allow for the large amounts of obsolete pesticide stockpiles and poisoning incidences is that none of the countries are members of the Organisation for Economic Cooperation and Development (OECD) (Davis 2002). Other factors also include the lack of expertise and knowledge to safely handle and dispose of the obsolete pesticides and also due to the lack of infrastructure.

As the above statistics reflect, obsolete pesticides pose a grave danger to humans. Furthermore, almost all of the obsolete pesticides are stored in containers that degrade over time. If the pesticides are left alone and the containers are allowed to degrade further, the pesticides within will leak into the soil, nearby streams and all groundwater zones at faster rates. If these huge stockpiles of obsolete pesticide remain in storage and are not dealt with safely, the numbers of poisoning and deaths will keep on rising.

Pesticide use has also a detrimental side effect on animal and plant life. Most of the pesticides work very well on most target pesticides; however they can also pose a threat to other flora which is beneficial to the environment and indeed beneficial to the crops. Their toxic effect can also affect other animal life, such as livestock, marine life and birds. This is particularly true in the case of the older pesticides which have a tendency to persist in the environment long after the crops have been harvested. This causes for the land to be contaminated for months or even decades depending on what pesticide was used.

The threat that obsolete pesticides pose has been recognised for decades and since the early 1990s a few initiatives have been tackling the problem but they have only been successful to a small degree. It became evident that a wider approach was required to increase pesticide awareness, disposal efforts and to prevent the reaccumilation of pesticide stocks.

In 2000 the Pesticide Action Network (PAN) and the World Wildlife Fund (WWF) recognised that a change in approach was required to efficiently tackle the obsolete pesticide problem and in December of that year the Africa Stockpiles Programme (ASP) was established. The aim of the ASP is to effectively and

safely remove all the stockpiles of obsolete pesticides from Africa and to place measures to ensure no further accumulation of pesticides occur.

The ASP has already begun tackling stockpile pesticides and some of the first countries to have their stockpiles of pesticides enumerated are listed below.

Table 1.3 - Data on Stockpiles of Obsolete Pesticides in African Countries in 2001.

Country	Pesticides (tonnes)	Examples of Pesticides
Ethiopia	3,400	2,4-D, DDT, Endosulfan, Malathion, Lindane
Mali	14,00	DDT, Dieldrin
Morocco	2,300	Carbaryl, DDT, Lindane, Heptachlor
Nigeria	21	Carbofuran, Dieldrin, Endosulfan, Lindane
South Africa	70,000	Hexachlorobenzene, Dieldrin, Lindane
Tanzania	1,200	Atrazine, Aldrin, DDT, DNOC, Toxaphene
Tunisia	1,000	Carbaryl, Fenitrothion, Lindane, Malathion

1.5 Pedology

Pedology is defined as the study of soil. The word soil is a very vague noun used to describe the land mass beneath people's feet. Soil is a very complex matrix with a wide variety of constituents that affect its character. Soil is generally defined as a natural body consisting of layers (soil horizons) of mineral constituents of variable thicknesses, which differ from the parent materials in their morphological, physical, chemical, and mineralogical characteristics (Birkeland 1999). All soils are derived from rocks that have been altered and degraded as a result of interacting with the climate and indigenous organisms. The rocks from which soils are formed from are called the parent rock; the rocks maybe limestone, sand, peat etc. However the term parent rock is not usually used by soil scientists who prefer to use the term parent material to avoid too liberal interpretation of the term "rock" (Jenny 1994).

The basic framework of pedogenesis can be expressed as follows:

Parent Material $\xrightarrow{\text{Soil Forming Factors}}$ **Mature Soil**

The soil forming factors are climate, organisms, topography, parent material and time. Climate regulates soil formation mainly through temperature and rainfall; areas with high rainfall and warm climates usually yield highly developed soils. This is due to the increased chemical weathering and by also influencing organisms' action on the soil. Organisms are more active in areas with warm climates. Organisms that live on and within the soil have an important role in soil formation. The soil forming organisms include trees and plants, animals, insects and microorganisms. An example of this soil formation is the formation of Inceptisol. Inseptisol is an order of soil that is created by the action of coniferous trees on the soil. Coniferous trees have acidic leaves and when they shed their leaves onto the ground, they create acidic leaf litter. These acidic conditions interact with the surface to create a specific kind of soil called inceptisol. Other example of organism related soil formation is the action of microorganism on the parent material. The decomposing action of soil bacteria on organic matter within base-rich parent material produces the soil order Mollisols.

The actions of the topography of the land and time are also an important factor. Topography dictates what sort of conditions effect certain areas, for example, low lying areas receive and retain more rain than elevated areas. This high rain exposure alters the parent material. Elevated areas also are affected due to the lower temperatures they are exposed to. The rate of chemical weathering increases about 2 to 3 times for every $10°C$ increase in temperature. Therefore lower regions usually have more developed or mature soils.

Soil cannot be easily categorised or defined. There are many different types and combinations of parent materials and many different soil forming factors which act up on them. Therefore, this is important to understand the behaviour and mechanochemistry of a wide variety of soils in order to cover most types of soil orders to produce a large reference point for the mechanochemical remediation of various soils.

It is also important to note that soil texture and porosity (soil micromorphology) are both important factors of soil health. The topsoil structure needs to have varying degrees of porosity to both absorb water for plants life to utilise and to circulate oxygen through. Furthermore, soil microbes also play an import role in determining soil health. They are involved in breaking down organic matter in a process called humification which produces humus which is described as mature compost. Topsoil with large organic matter content is also referred to as humus. This topsoil is very fertile and is agriculturally important to humans.

Therefore, it is important to understand how soil bacteria behave in soils in general and particularly in soils that are contaminated and undergone remediation.

1.6 Soil Microbiology

The macro and microbiology of a soil are of great importance in terms of soil fertility and its ability to sustain plant life. The lifecycles of the organisms directly affect the soil and conditions it to support plant life.

Soil bacteria breakdown organic matter that would otherwise litter the soil, and also enhances nutrient availability for plant life uptake. This bacterial

biodegradation also improves the soil's micromorphology. They breakdown soil structures which re-aggregate them allowing for better porosity.

Soil bacteria can be grouped into five main categories (Reid 2005):

1. Decomposers
2. Disease suppressors
3. Nitrogen Fixers
4. Sulfur oxidisers
5. Actinobacteria

Bacteria from each group play a vital role in promoting healthy soils.

The decomposers are responsible for breaking organic matter and releasing nutrients for plant uptake as mentioned earlier. An example of decomposing bacteria is *Bacillus subtilis* (Reid 2005).

Disease supressing bacteria, as their name suggests help supress plant diseases. Some examples of disease supressing bacteria are:

- *Bacillus subtilis* which supresses seedling blight of sunflowers caused by *Alternaria helianthi* (Reid 2005).
- *Bacillus megaterium* has been used to supress the disease-causing fungus *Rhizoctonia solani* (Reid 2005).
- *Pseudomonas fluorescens* has also been found to be useful against *Rhizoctonia solani* (Reid 2005).

Nitrogen fixing bacteria are able to extract nitrogen gas from the air convert it into ammonia which is then utilised by the plants. This process is essential for life because nitrogen is required for the biosynthesis of nucleotides which are the building blocks of DNA and RNA and of amino acids which are the building

blocks of protein (Postgate 1998).Sulfur oxidising bacteria play a similar role to the nitrogen fixing bacteria; they make sulfur available for plant uptake. Many soil minerals contain sulphides but sulfur in the form of sulphides cannot be utilised by plants (Reid 2005). Sulfur oxidising bacteria are able to convert sulphides into sulfates and in this form, plants are able to utilise them. Thiobascillus bacteria are some of these sulfur oxidising bacteria.

1.7 Thesis Rationale

The aim of this study was to further develop the understanding and mechanisms of the mechanochemical remediation of land contaminated with organic pollutants. As described earlier in this chapter, pesticides pose a huge environmental risk, especially in developing countries which have huge stockpiles of obsolete pesticides. The study examined the effects of different soils have on the destruction of organic pollutants and it will also look into the effects of water and organic matter content on the destruction rates. Water is known to hinder the destruction of pollutants, but it is not known why or how it does so and whether indeed water levels and destruction rates are inversely proportional or not. Furthermore, the study also examined the impact MCD technology has on soil bacteria, soil structure and how fertile soil is (ability to sustain plant life). As mentioned earlier, soil bacteria, porosity and texture are important factors of soil health. Therefore it was important to see whether soil that has undergone the MCD process would suffer from any sort of deleterious effects that would alter its structure and or completely remove beneficial bacteria.

For the MCD process to be successful, it is important to know how varying soil compositions, constituents, organic content and water concentration behave

during milling. Information on the mechanochemical destruction efficiency of organic pollutants in a wide range of soil types would make it easier to make a decision whether the MCD process would be suitable to remediate a particular soil. Soil is a very complex matrix, with organic and inorganic materials that dictate its porosity, oxygen content and mineral profile. A tool used to help classify soils is called a soil texture triangle (fig. 1.2). The sides of the soil texture triangle are scaled for the percentages of sand, silt, and clay. Clay percentages are read from left to right across the triangle. Silt is read from the upper right to lower left. Sand is read from lower right towards the upper left portion of the triangle. The boundaries of the soil texture classes are highlighted by colour. The intersection of the three readings on the triangle gives the texture class. Therefore a variety of soils types with varying textures were studied in an effort to obtain data on destruction efficiency versus soil type.
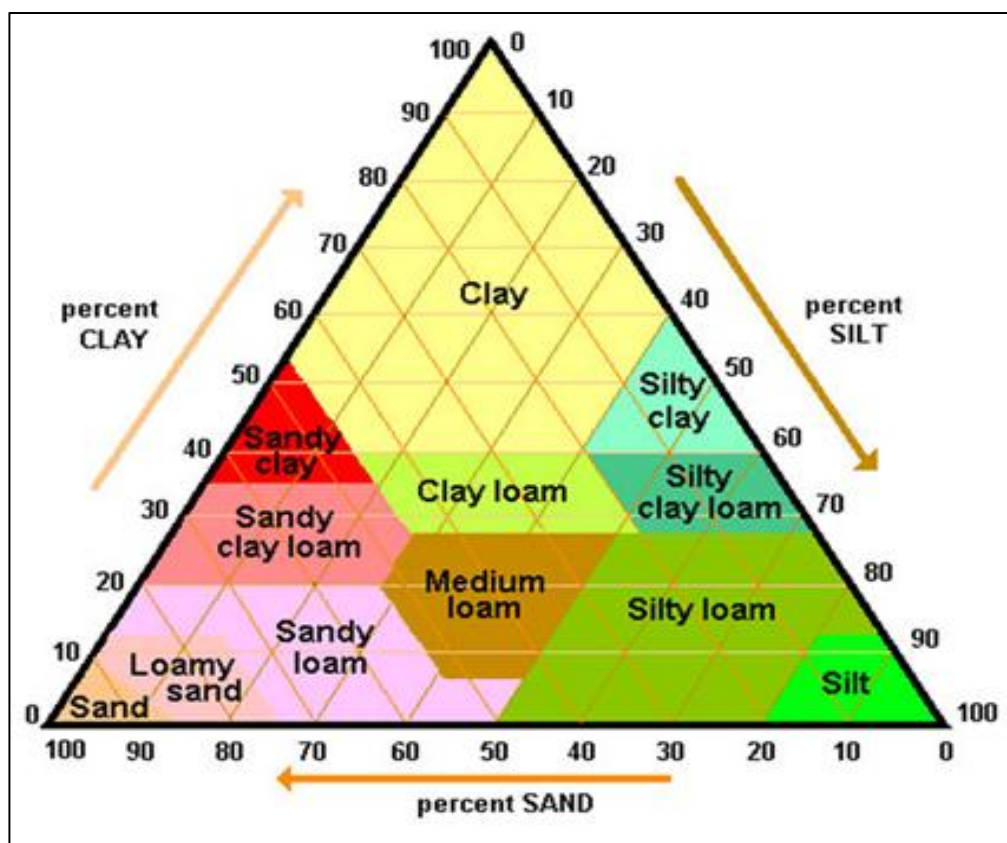
Figure 1.2 – Soil texture triangle

The ASP, FAO, WWF and PAN have pooled their resources in the fight against obsolete pesticides and the reported costs are very high. For the most part, remediating contaminated land is a complex under-tacking which depends on complex infrastructure. A quick review of the other available decontamination technologies has suggested that most have either economic and/or functional barriers which render them to be unfeasible options for many situations.

The mechanochemical destruction (MCD) technology is a method which allows for the remediation of land contaminated with organic pollutants which does not rely on any sort of large and complex infrastructure and is relatively inexpensive. The MCD method proves to be an attractive option for countries with low resources and is also an option for developed countries like New Zealand in need for a more cost effective remedial solution. It is also an ideal solution for the obsolete pesticide stockpiles problem in Africa as it has proved to be a fast, cost effective and relatively simple method for remediating soils contaminated with organic pesticides.

Chapter 2 - Soil Remediation Technologies

The contamination of subsurface soil all over the world is a serious and challenging problem, particularly in developing countries or highly industrialised areas (Rivas 2009). Some of the main contaminates found in soil and groundwater includes arsenic, cadmium, mercury, lead, Polycyclic Aromatic Hydrocarbons (POP), Polycyclic Chlorinated Biphenyls (PCB) and Polycyclic Aromatic Hydrocarbons (PAH) (Bellingham, 2005). Soils can be contaminated with heavy metals derived from numerous sources including abandoned mining wastes, leakage of landfill leachate and improper treatment of industrial wastes (Adriano, 1986). All of the fore mentioned contaminants are toxic to people. A study by Perera et al., 2009 have found that high prenatal exposure to PAH be associated with lower IQ (Perera, 2009). PAH toxicity is dependent on its structure; its isomers can be nontoxic to extremely toxic. Some PAHs known for their carcinogenic, mutagenic and teratogenic properties are chrysene , benzo[b]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, and ovalene (Luch, 2005). It is therefore vital for human health and longevity to develop techniques which can remove such toxins from land safely, permanently and inexpensively.

Contaminated soil remediation technologies can be broadly divided into three main groups (Virkutyte 2002):

    1.   Thermal remediation

    2.   Biological remediation

    3.   Chemical remediation

Each group has a variety of methods and each of these methods have their advantages and disadvantages.

2.1 Thermal Remediation Technologies

Thermal remediation technologies use high temperatures to degrade toxic materials. The high temperatures greatly accelerate oxidation, reduction and pyrolysis reactions. The temperatures required to initiate such accelerated reactions are often well over 1000°C. These high temperatures allow for fast and close to complete pyrolysis of the target toxins and also ensure a fast and efficient throughput.

Thermal remediation technologies are very versatile; they are able to degrade a wide variety of chemicals, wastes and pollutants. It can also treat waste in various forms, from solid, liquid to gas and can also handle waste or pollutants that are sequestered or integrated into a matrix like organic pollutants in soil.

There are many different incineration techniques such as vitrification, plasma arcs, and cement kilns.

Thermal remediation techniques are very fast and efficient; however they have two major drawbacks: High energy consumption and emissions containment.

Due to the high temperatures required to treat chemicals and pollutants, a lot of energy is required to generate this heat. This in turns drives operation costs up.

Thermal remediation technologies remediate large amounts of chemicals per cycle in order to maximise remediation and cost efficiency, this high throughput makes it difficult to contain the generated products and gas phase reactants. To contain all the emissions, large complex infrastructures are required to contain, monitor and control the entire process safely. This also drives up the operating cost as building such large ex-situ installations is very expensive.

The cost of incineration in the USA is up to USD$1,500 per tonne for halogenated organics and up to USD$1,000 per tonne for contaminated soil (USEPA, 2000). For the disposal of obsolete pesticides from developing countries by incineration the cost is at least USD$3,000 per tonne due to the extra handling and transport of the pesticides.

Thermal incineration is the most popular remediation method worldwide, however in recent years opinions have shifted as concerns about dioxin emissions have been brought to attention.

Three dioxin formation pathways (McKay 2002):

(i)   From polychlorinated dibenzodioxins and polychlorinated dibenzofurans originally present in the furnace feedstock.

(ii)   From precursor compounds (foundation formatting molecules which could react rapidly with other groups in the system to form dioxins) in the waste feed.

(iii)   From de novo synthesis of smaller, relatively innocuous chemical molecules combining together to form the dioxins.

Dioxins and furans form during cooling of the stack gases between 600°C and 200°C. The formation of these compounds has been minimised in modern incinerators by quenching off-gases quickly to below 200°C and by passing off-gases through extensive gas cleaning processes (Bellingham 2005), but opinions are still very much divided on the safety of the technology.

2.1.1 Vitrification

Vitrification is a process that involves melting contaminated soil between an array of electrodes. As electricity passes through the soil, heat is generated and the soil begins to melt when the temperatures reach a range between 1,500°C – 2,000°C (Bellingham 2005). Once the desired area has become molten, the electricity flow is shut off and the molten soil is left to cool into a solid vitreous mass resembling obsidian. This process is extremely efficient reaching over 99% of organic pollutants destroyed (Fraser 2001). The vitreous mass (fig. 2.1) also sequesters any surviving pollutants as the vitrified product is chemically inert, generally neutral in pH and exhibits excellent leach properties.
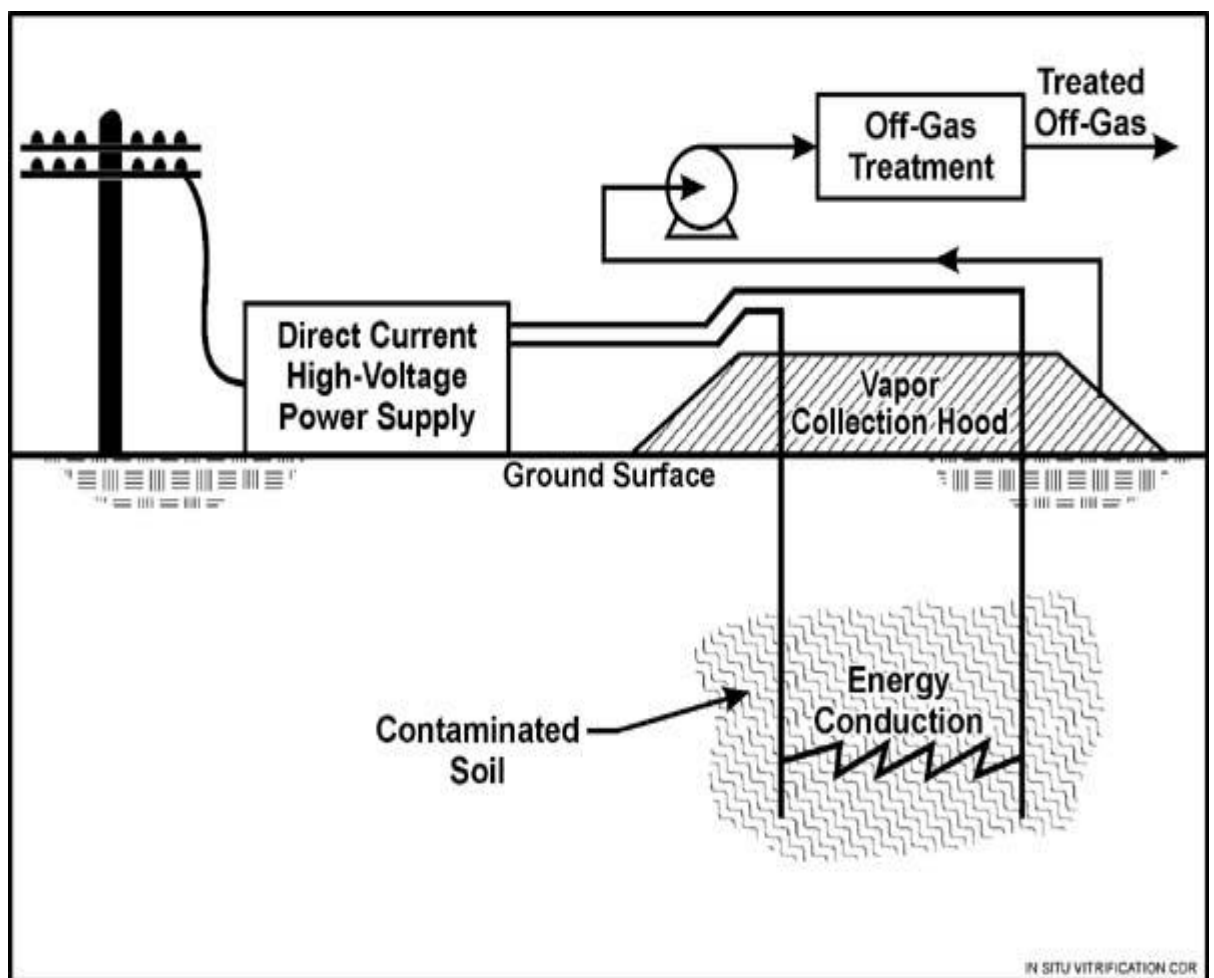
Figure 2.1 - Vitreous Process Schematic (Courtesy of NAVFA)

2.1.2 Plasma Arc

As the name suggests, the plasma arc process utilises generated plasma to incinerate wastes and pollutants. Plasma is generated by directing electrical currents through a gas stream and then wastes and pollutants are injected directly into the plasma stream.

Within a contaminated soil context, divided soil packets are injected into the plasma which becomes vitrified due to the high temperature of the plasma.

Plasma reaches a temperature range between 5,000°C – 15,000°C which can dissociate the wastes and pollutants into its atomic elements (Bellingham 2005).

Large amounts of power are required to generate the electrical currents used to generate the plasma arcs; however this energy can be re-harnessed by collecting the steam and gases produced by the process. The steam and gas (after being cleaned) are directed to a steam turbine to generate electricity and it is also possible to turn the steam into distilled water after a multi effect distillation process (fig. 2.2).
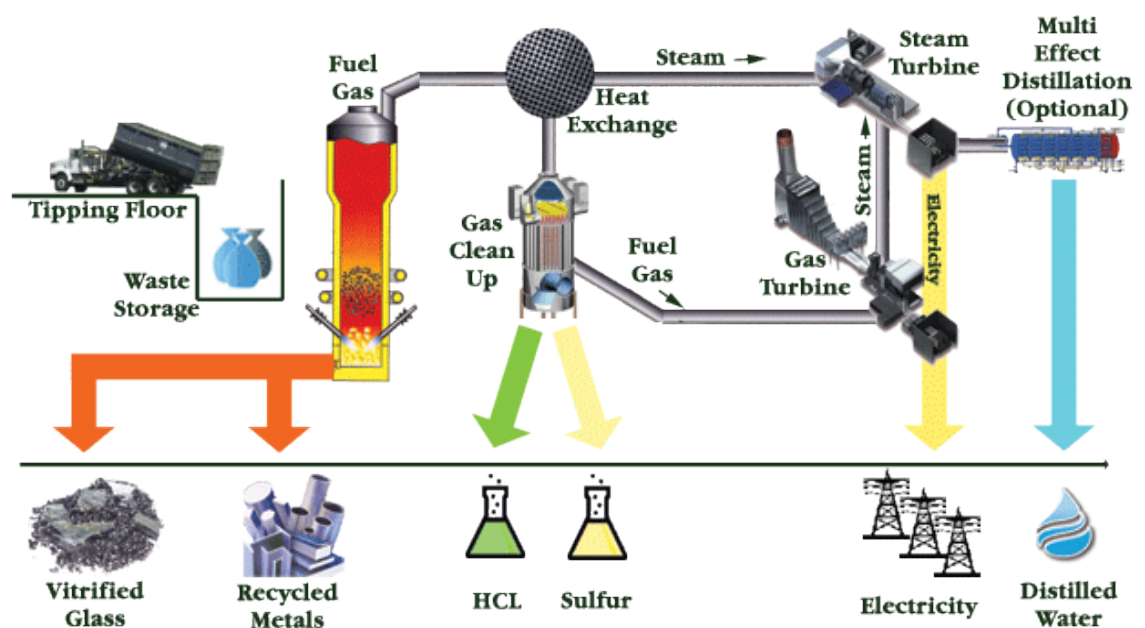
Figure 2.2 - Plasma Arc Waste Disposal Flowchart (Courtesy of Tech-Faq).

2.1.3 Cement Kilns

Cement kilns are designed for the pyro-processing stage of cement manufacture. The kilns are large cylinders that rotate on an incline, the elevated end is where the material is fed in and the lower end is heated. This action allows for the material fed into the kiln to heat up and mix together. To manufacture cement, a mixture of limestone and clay (raw-mix) is fed into the rotating kiln. The raw-mix travels to the lower end of the kiln where it is exposed to sintering temperatures of around 1,500°C. The resulting product is then grounded to produce cement. Within the context of contaminated soil remediation, the cement kiln can be used to remediate soils contaminated by organic pollutants (chlorinated organic waste), but must be slightly modified. The contaminated soil cannot be fed into the elevated entry point as the temperature is too low; allowing for the waste to volatilise and not be adequately destroyed (Rahuman 2000). The kiln would need to have an entry point installed in the middle where the temperature is high enough for complete destruction of any contaminant.   The destruction of organic contaminants in modified cement kiln can reach 99% completion (Benestad 1989).
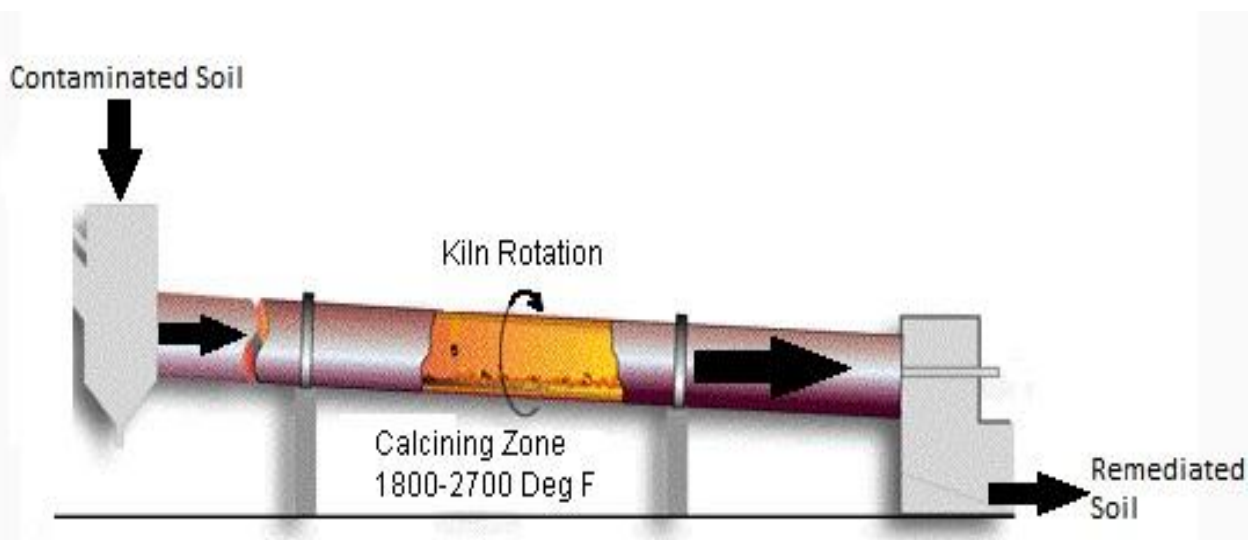
Figure 2.3 – Cement Kiln Schematic (Courtesy of mine-engineer.com)

2.2 Biological Remediation Technologies

Bioremediation is a remedial process which utilises biological agents to remediate contaminated land. Naturally occurring metabolites and enzymes from microorganisms and plants are used to catalyse detoxification reactions (Glazer 1995).

Bioremediation methods can either be classified as in situ or ex situ and either be intrinsically or artificially. There are many different types of technologies that fall under the bioremediation technology banner. Some of the techniques include phytoremediation and mycoremediation.

Biological remediation technologies have a number of advantages and few disadvantages. Bioremediation can be utilised in areas where accessibility is difficult or excavation in impractical. It is relatively inexpensive, non-invasive, aesthetically pleasing and is considered a "green" remedial solution.

It however also has a few disadvantages; most techniques take a long time to take effect (especially phytoremediation), site that have been bioremediated require long term monitoring, poor bioavailability of chemicals, presence of other toxic compounds, inadequate supply of nutrients and insufficient biochemical potential for effective biodegradation (Dua 2002).

2.2.1 Phytoremediation

Phytoremediation is a form of bioremediation that utilises plants that mitigate the contaminated soil situation directly without the need of any chemical or physical (excavation) intervention. The process subsists of mitigating the concentrations of contaminants in environmental matrices like soil water and/or

air using only plants with the ability to sequester, denature or eliminate the targeted contaminants. Phytoremediation has been classified into five main subgroups (Pulford 2002):

1. Phytoextraction: plants remove metals from the soil (fig. 2.4) and concentrate them in the harvestable parts of plants (Kumar 1995).

2. Phytovolatilisation: volatilisation of pollutants into the atmosphere via plants (Ban˜uelos 1997; Burken 1999).

3. Phytodegradation: plants and associated microbes degrade organic pollutants (Burken 1997).

4. Phytostabilisation: plants reduce the mobility and bioavailability of pollutants in the environment either by immobilisation or by prevention of migration (Vangronsveld 1995; Smith 1972).

5. Rhizofiltration: plant roots absorb metals from waste streams (Dushenkov 1995).

Examples of phytoremediation plants:

Table 2.1 – List of phytoremediation plants

Ambrosia artemisiifolia	Lemnaoideae	Reed canary grass
Apocynum cannabinum	Melastoma affine	Salix babylonica
Barley	Moringa oleifera	Sunflower
Brassica juncea	Panicum virgatum	Tradescantia pallida
Carex nebrascensis	Pennisetum purpureum	Thlaspi caerulescens
Festuca arundinacea	Phragmites	Vicia faba
Hydrilla	Pistia	Wolffia arrhiza

Advantages of phytoremediation:

- Monitoring of the plants can be done easily. Measuring indicators like pH, soil extraction and electron/proton donors can track the remediation process.

- It is aesthetically pleasing. No machinery and equipment is required to remain on site, only thing that remains are plants.

- It is relatively much cheaper than other in situ and ex situ technologies.

- It is the safest and least harmful remediation method.

Disadvantages of phytoremediation:

- Danger of passing pollutants e.g. heavy metals into the food chain by livestock that have grazed on plants with bio-accumulated contaminants.

- Depth of remediation is limited by the length of the remediating plants' roots.

- Severely contaminated soil can be too toxic for remediating plants to survive long enough to remediate the area.

- Slow process due to slow plant growth and low biomass.

- The slow nature of plant based remediation allows for contaminant leaching.
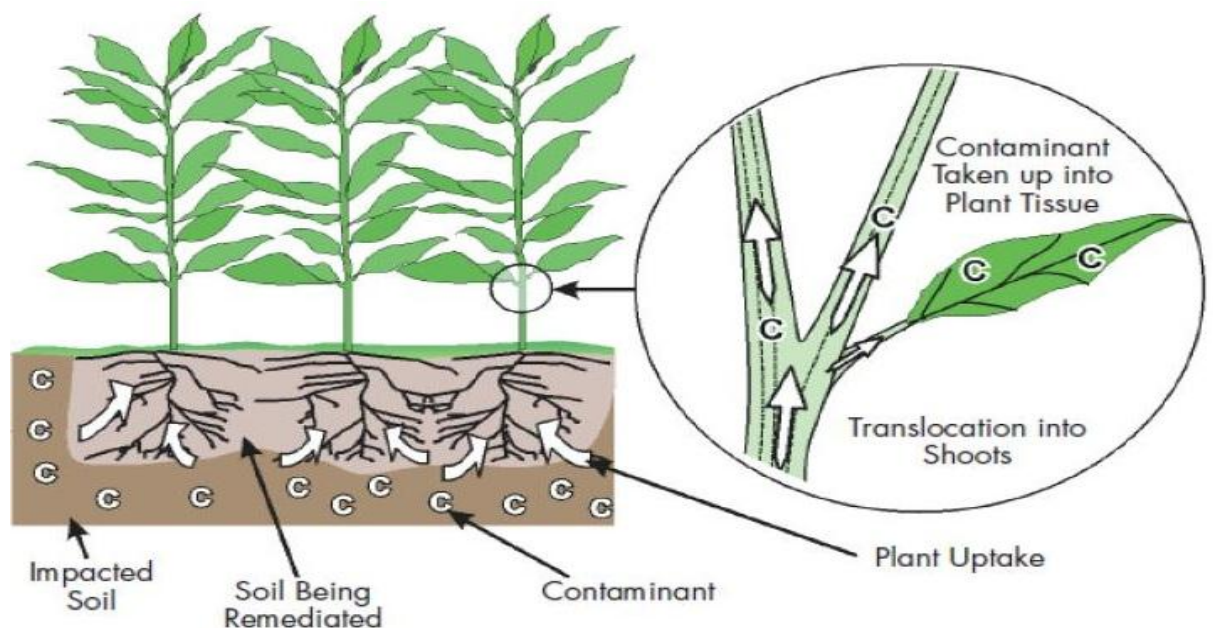
Figure 2.4 – Phytoextraction of contaminants from soil. (Courtesy of Biology-Online)

2.2.2 Mycoremediation

Mycoremediation is a method of decontaminating soil by using fungi. The process utilises fungi's natural processes to sequester or degrade contaminants in soil. Fungi are able to achieve this by stimulating enzymatic and microbial activity which degrades organic pollutants. Unlike plants, fungi are not autotrophs; they cannot produce their own complex organic compounds like carbohydrates (glucose) to feed on. Fungi are heterotrophs and must obtain all their nutrients from external sources. This is done by the fungi's mycelia which are the vegetative part of the fungi that consist of hyphae (fig. 2.5). These hyphae secrete enzymes onto organic matter in the soil which break them down from polymers to monomers in order to make it easier to absorb via active transport and facilitated diffusion.

This natural heterotrophic action can be used to breakdown organic pollutants within the soul. The enzymes that are secreted from the hyphae can also degrade organic based pollutants. Bhatt et al. studied the degradation abilities of two white-rot fungal culture strains of Irpex lacteus and Pleurorus ostreatus on seven three and four ring unsubstituted aromatic hydrocarbons (PAH) in two contaminated industrial soils. Respective data for removal of PAH in the two industrial soils by Irpex lacteus were: fluorene (41% and 67%), phenanthrene (20% and 56%), anthracene (29% and 49%), fluoranthene (29% and 57%), pyrene (24% and42 %), chrysene (16% and 32%) and benzo[a]anthracene (13% and 20%) (Bhatt 2002). In the same two industrial soils Pleurorus ostreatus degraded the PAH with respective removal figures of fluorene (26% and 35%), phenanthrene (0% and 20%), anthracene (19% and 53%),

fluoranthene (29% and 31%), pyrene (22% and 42%), chrysene (0% and 42%) and benzo[a]anthracene (0% and 13%) (Bhatt 2002).

Another method of mycoremediation is to use specific species of fungi that are classified as hyperaccumulators. Hyperaccumulating fungi have the ability to absorb and sequester heavy metals from the soil (similar to phytoextraction). Great efficiency in detoxification and sequestration is a key property of hyperaccumulators which allows them to concentrate huge amounts of heavy metals in their organs without suffering any phytotoxic effect (Rascio 2011).
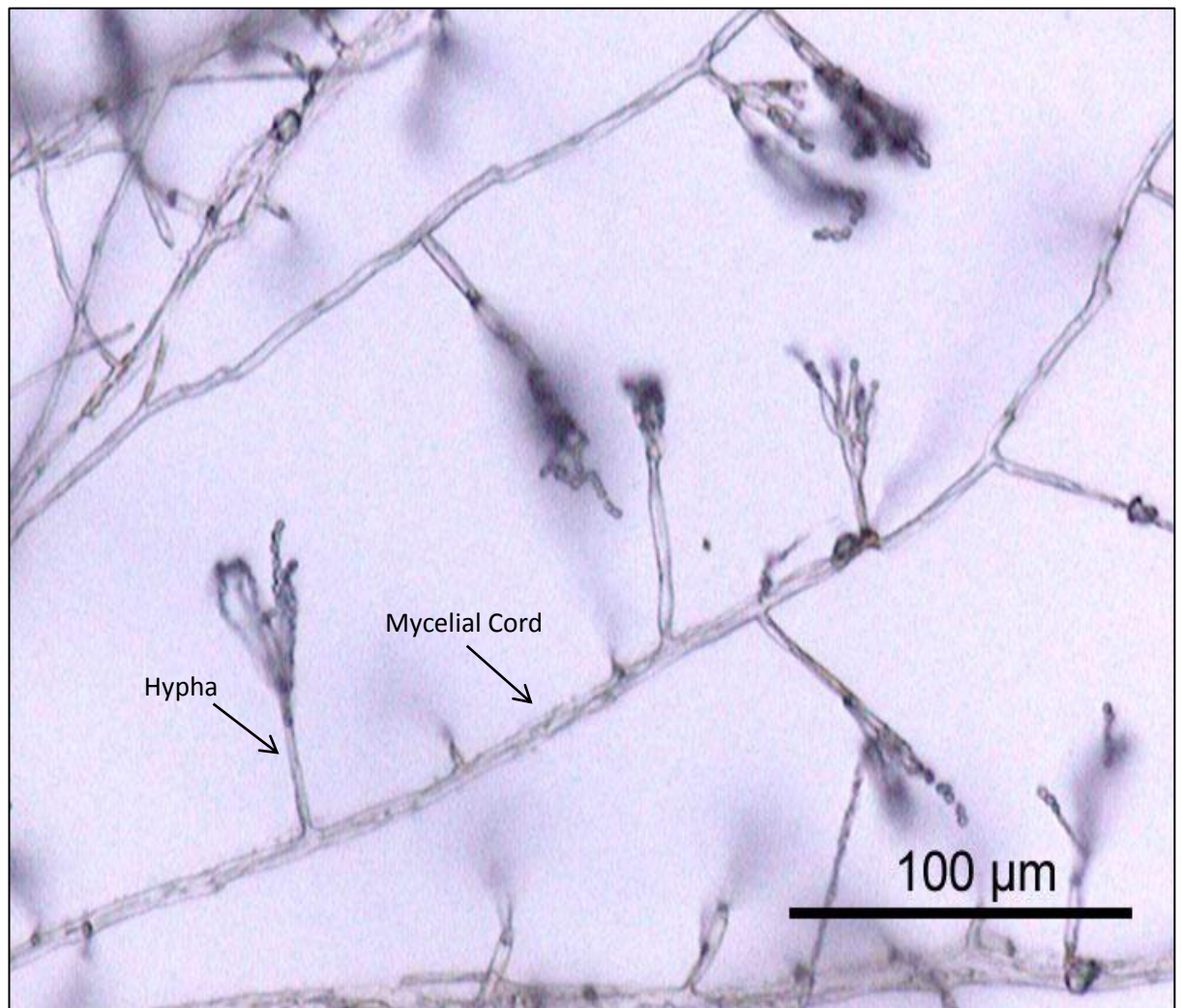
Figure 2.5 – Microscopic of view of Penicillium mycelium (Courtesy of Wikipedia)

2.3 Chemical Remediation Technologies

Chemical remediation utilises powerful oxidation and reducing agents to react with contaminants to yield benign products. Chemical remediating reactions can be reasonably fast but in some instances can be rather slow like in the case of chlorinated aromatics (Bellingham 2005). Reaction rates can be accelerated by use of catalysts and by adding energy in the forms of radiation, solar, heat, electrical and kinetic.

Chemical remediation technologies often use small portable equipment which allows in situ remedial works. This brings down costs as no fixed facilities or excavation and transportation of the contaminated soil is required. Furthermore, chemical remediation technologies can operate as batch processes which also reduces cost and complexity (Bellingham 2005).

The control of chemical reaction is usually easy to control and the potential of emissions escaping is quite low, making most chemical remediation methods relatively safe to both people and the environment.

However, the strongly oxidizing and reducing agents required must be handled with great care. Measures must be taken to shield the reactants from the atmosphere; the use of inert substances to shield the reactants from the atmosphere is a common method of achieving this.

Some chemical remediation technologies are Fenton's reagent, sorptive/complexing remediation, and electrochemical remediation.

2.3.1 Fenton's Reagent

Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidise contaminants. The catalytic activity of ferrous and cuprous ions in the dissociation of hydrogen peroxide molecules is basic mechanism of Fenton's chemistry (Bellingham 2005). Catalysed decomposition of hydrogen peroxide (H2O2) by iron (II) to form hydroxyl radicals (OH•):

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^• \qquad \text{Equation 2}$$
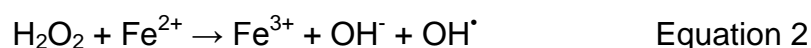
Fenton's reagent was developed in the 1890s by Henry John Horstman Fenton as an analytical reagent (Fenton 1894).

This technique high highly versatile and is able to remediate soils contaminated with wide a range of contaminants. Certain conditions are required for this technique to perform well like pH levels and temperature. Optimum pH level is from 3 – 7 and it was also reported that total organic carbon removal increases as temperature increases (Bellingham 2005).

Soil type and organic content also have an effect on the destruction efficiency of contaminants by the Fenton method. A study by Kojima et. al looked at the destruction rates of trichloroethylene by oxidation via Fenton's reagent in different soils. They demonstrated that the destruction rates of trichloroethylene decrease in most of their test soils and speculated destruction kinetics are affected by both specific surface area and carbon content of the soil (Kojima 2009).

2.3.2 Sorption and Complexation

Sorption refers to a process where absorption and adsorption occur simultaneously. In adsorption, atoms or molecules accumulate on surfaces of materials. This process creates a film of the adsorbate on the adsorbent's surface. Absorption is a chemical and/or physical process where atoms, ions or molecule enter a solid, liquid or gas matrix and becomes a part of it. Therefore, sorption is the effect of gases or liquids being incorporated into a material of a different physical state which then adhere to the surface of another molecule.

Adsorption can be approximated by the equation: $Kd = Cs / Caq$, where Kd is the partition or distribution coefficient, Cs is the quantity adsorbed per unit amount of solid and Caq is the concentration in the aqueous phase (Deutsch, 1997). As the amount of adsorbed in a system increases, it becomes more difficult for further adsorption to continue. If this happens, then the Cs/Caq relationship may not be linear (Deutsch, 1997).

A 2005 study by Shirin et al. looked at enhancing the solubility of organic pollutants through complexation by cyclodextrins (cycloamylose). Cyclodextrins are a group of cyclic oligomers of glucose in the normal C-1 conformation in which the individual glucose units are connected by 1,4 bonds (Shirin, 2005). In water, cycloamyloses form 1:1 complexes with many organic molecules and most benzenoid derivatives. X-ray and spectroscopic evidence indicates that the guest molecule such as pollutants (usually a small organic molecule) is bound tightly in the cavity of the host molecule (the cycloamylose) just like a key fitting into a lock. The result is an inclusion complex, which is what is formed by enzymes when they first bind the molecules whose reactions they subsequently catalyse. Substituted cyclodextrins in which one or more hydroxyl groups have

been modified with e.g. –CH3 and –CH2COO- have many desirable properties compared with unmodified cyclodextrin, including greater aqueous solubility and binding ability (Shirin, 2005). Shirin et al. determined that selected cyclodextrins are capable of effective removal of perchloroethylene and trichloroethylene from soil samples.

2.3.3 Electrochemical Remediation

The theories behind electrochemical remediation are not new. A German medical doctor and researcher named F. F. Reuss discovered the phenomena of electroosmosis and electrophoresis in 1809 while working at the University of Moscow. His work was published in both French and Latin in the journal Memoires de la Societe Imperiale des Naturalistes de Moscou (Reuss 1809).

Electrokinetic remediation utilises five electrokinetic phenomena to remove heavy metals from soil-water mixtures:

1. Electroosmosis: Movement of water through a solid matrix under an electric field

2. Electrophoresis: Movement of suspended particles through water under an electric field

3. Streaming potential: Small electric field caused by the movement of water through a soil matrix

4. Sedimentation potential: Small electric field caused by movement (sedimentation) of solid particles through water

5. Electromigration: Movement of cations and anions under an electric field

Within the context of heavy metal contaminated land remediation, only two of the above phenomena are really relevant; electroosmosis and electromigration.

Electroosmosis

- Electroosmosis is defined as the movement of water through a matrix due to the effect of an applied electric field (Reuss 1809).

- Water molecules are polar i.e. the water molecule forms an angle, with hydrogen atoms at the tips and oxygen at the vertex. Since oxygen has a higher electronegativity than hydrogen, the side of the molecule with the oxygen atom has a partial negative charge.

- This electronegativity will result in the water molecule to be attracted to the positively charged electrode i.e. the anode (fig. 2.6).

- This flow of water to the anode will flush out heavy metals and even organic contaminants.

Electromigration

- Electromigration is defined as the attraction and migration of charged ions to either an anode or cathode depending on the ion's intrinsic charge.

- When ions are dispersed within a medium and an electric field is applied via two electrodes, any present anions within the medium will migrate to the anode and any cations present within the medium will migrate to the cathode (fig. 2.6).

- Electromigration requires the pH of the medium to be controlled due to the reactive nature of the ensuing hydrogen and hydroxide ions (Athmer 2007).
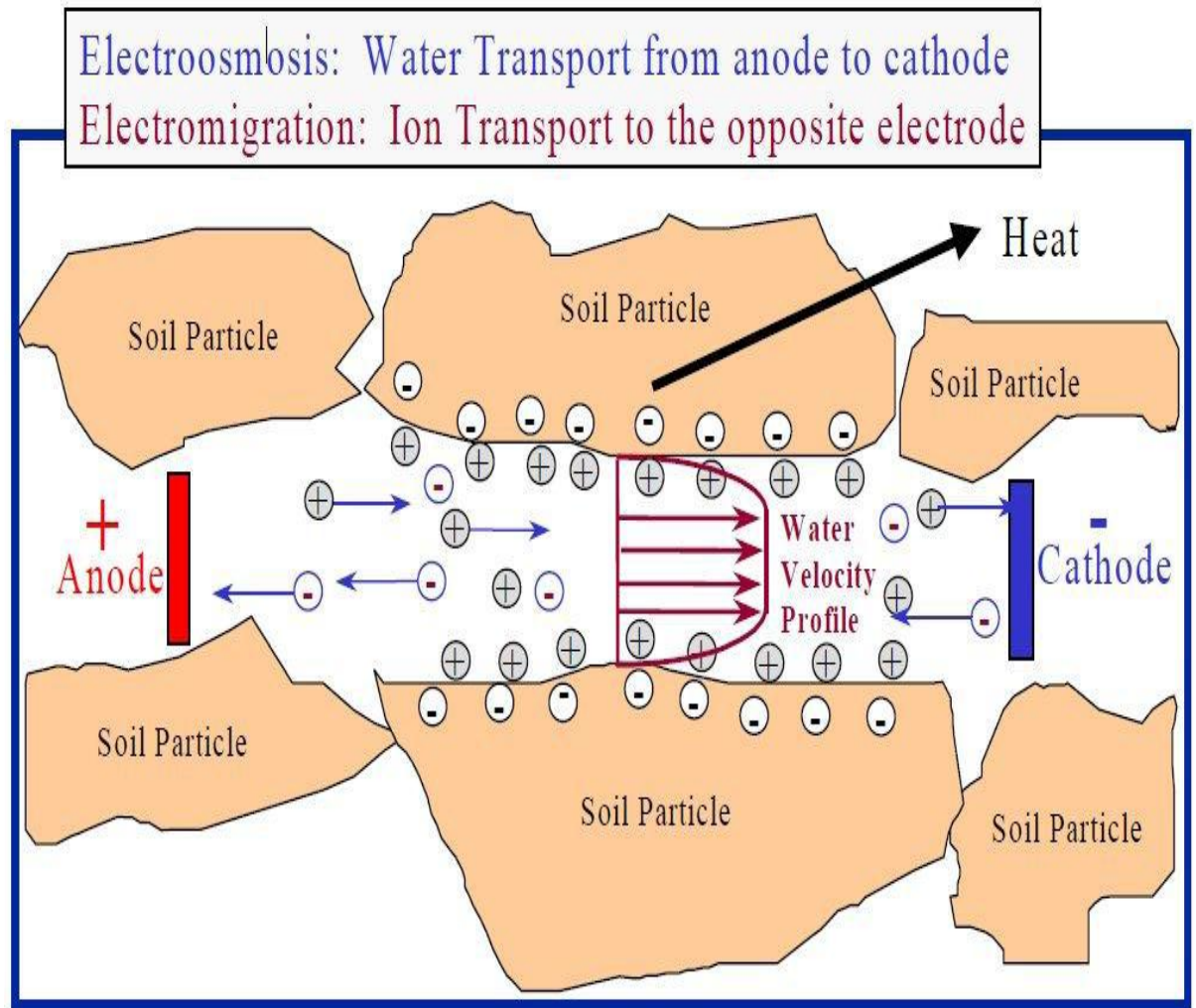
Figure 2.6 - Water molecules (osmosis) moving towards the cathode carrying contaminant along the way and anions migrating (migration) to the anode (Athmer 2006).

Electrokinetic remediation utilises direct current or low potential gradients applied to electrodes inserted in heavy metal-contaminated land (Probstein, 1993).

Heavy metals intrinsically carry either a negative or positive charge. Therefore, according to the charge of the heavy metal, it would travel through the soil towards the anode or cathode (Al-Hamdan, 2008).

Electrokinetic remediation uses two electrodes which are inserted at opposite ends in a site identified to be contaminated with heavy metals (fig. 2.7).
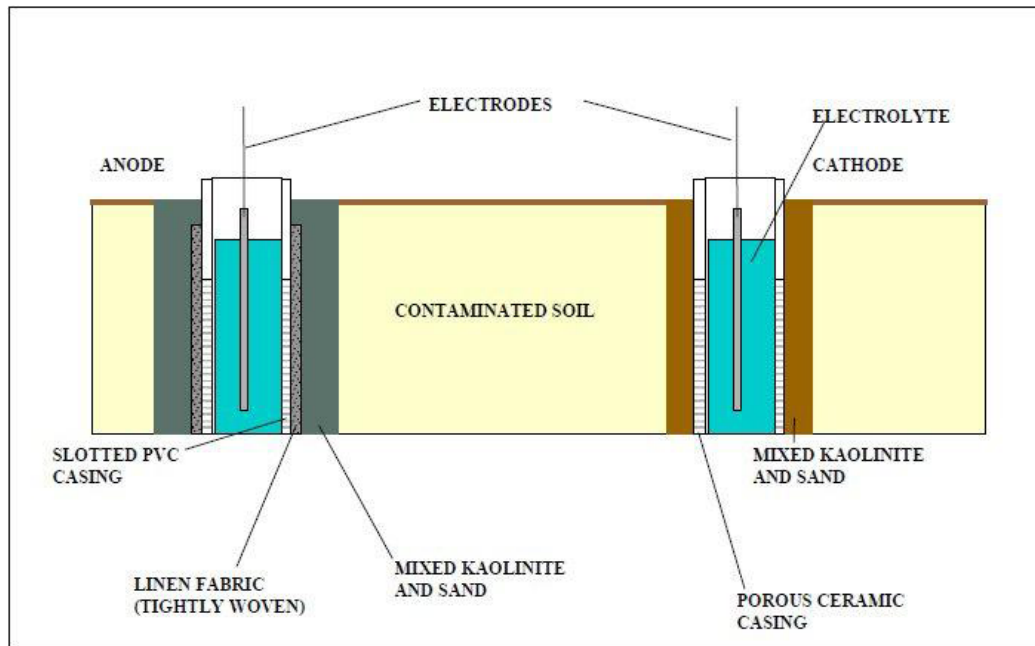
Figure 2.7 – Electrode assembly (USAEC 2000)

Direct current is used to create an electric potential between the two electrodes (Figure 2). The power supply used must be able to deliver currents of 3.5 A/m2 of cross sectional area between the electrodes and be able to produce a voltage potential of 35 to 105 V/m between the electrodes (Sharma 2004).

Before the electrodes are inserted into the heavy metal-contaminated land, wells must be built to accommodate them. The wells are usually constructed using perforated PVC piping or porous ceramic. The wells are usually wrapped in a geotextile; this would only allow water and heavy metals to flow into the wells. Once these wells are ready, the electrodes are lowered in (Kalumba 2006).

The cathode well is filled with deionised water until the water is level with the soil. This is done to facilitate the washing of the contaminant cations from the

anode across the specimen soil towards the cathode during the electroosmotic process (Kalumba 2006). The water at the anode well must be continually topped up to replace the electroosmotically flushed water.

At the cathode end, an effluent tube is connected to a pump to extract all the water and heavy metals that have leached from the soil into the cathode well. There are other techniques other than effluent pumping used to remove the leached heavy metals e.g. precipitation, complexation, electroplating and adsorption (Probstein, 1993; Mattson, 2000; Alshawabkeh, 2005). However, pumping the effluent water is the simplest and least invasive method.

As mentioned earlier, the two main phenomena that electrokinetic remediation utilises are electroosmosis and electromigration.

Electroosmotic flow occurs due to an electrical double layer that forms at the stationary/solution interface. Typically, the surfaces of soil particles are negatively charged. This negative charge will attract cations present in the pore water. The cations will align themselves along the negatively charged soil particles. This will in turn cause the water molecules to be attracted to the row of cations due to its polar nature and align themselves along the cations.

Due to the fact that water molecules outnumber the number of cations within the pore water, the cations cannot line all the negatively charged soil particles. When there are no excess cations, water molecules start aligning themselves on the remaining soil particles. Water molecules closest to the particles are held with more force due to their proximity to the attractive charge. The water molecules within this double layer (fig. 2.8) are able to move freely (Sharma 2004).
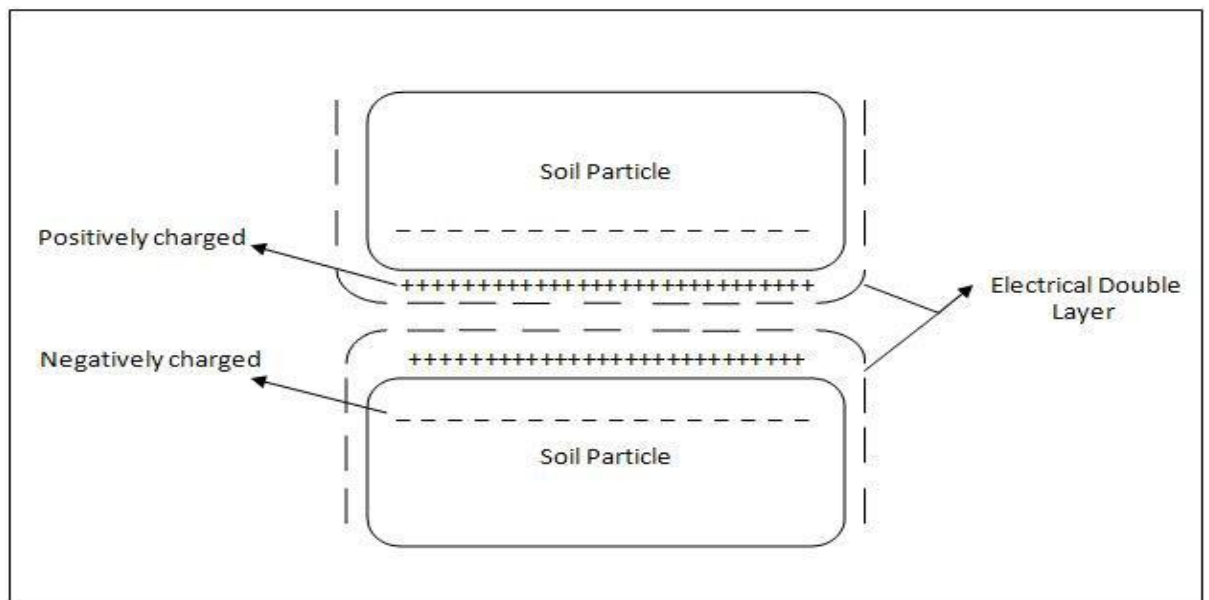
Figure 2.8 – Diagram of an electrical double layer

On the application of the electric field, water molecules will start to move towards the cathode. However, the movement of water molecules in the double layer is governed by the soil particles' zeta potential (Probstein 1993). The zeta potential is defined as the potential between the stationary and mobile components of the double layer surrounding the soil particles (Sharma 2004). Electroosmotic flow is also dependent on the viscosity of the pore water, ion concentration, mobility of ions and temperature (Mitchell 1993). In fine-grained soils, water flow due to electric gradients is a few orders of magnitude higher than water flow due to hydraulic gradients (Mitchell 1993). Therefore, electrokinetic remediation techniques are most effective when used in soils made up of fine grains with micrometre-sized pores (Acar 1993).The technology is applicable to a wide range of contaminants. It does not only remove charged ions, heavy metals and radionuclides (Reddy 1999), but also remove non-charged contaminants by the induced electroosmotic flow. It can also be used on different kinds of soils like heterogeneous and low-permeability soils.

Chapter 3 - Mechanochemistry

Many chemical reactions can be activated by energy. Many forms of energy can initiate these reactions; the most common forms are thermal and photo energies. Mechanochemistry is the study of chemical reactions which are initiated by mechanical/kinetic energy (Heineke, 1984).

Therefore, Mechanochemistry is the branch of chemistry dealing with the chemical and physicochemical changes of multi-state aggregated substances due to the influence of mechanical energy (Heineke, 1984).

The processes of mechanochemical reactions can be divided into three categories (Bellingham, 2005):

1.   Mechanical Milling

2.   Reaction Milling

3.   Mechanical alloying

The process of interest in contaminated land remediation is the reaction milling (RM). RM uses kinetic energy to break bonds of solids in order to allow reactions (organic and inorganic) to take place e.g. complex formation, REDOX and ion exchange (Steinike, 2000 Kaupp, 2005).

RM is achieved by placing contaminated soil in a ball mill and rotated at high velocities so that the balls within the mill can crash into the soil and disrupt the chemical composition of the targeted contaminants (figure 3.1). The mills used are very powerful, they are designed to put significant amounts of energy into the milled material creating a fluidised reactive cloud of mineral particles with a large number of electrons (inorganic free radicals) and ions on their surfaces (Robertson, 2008).

Ions, radicals and neutral molecules themselves bind to the reactive fracture surfaces and undergo similar fragmentations that the parent substrate underwent. The final products are small molecules including ethane, methane, carbon dioxide, hydrogen, water and carbon (Robertson, 2008).
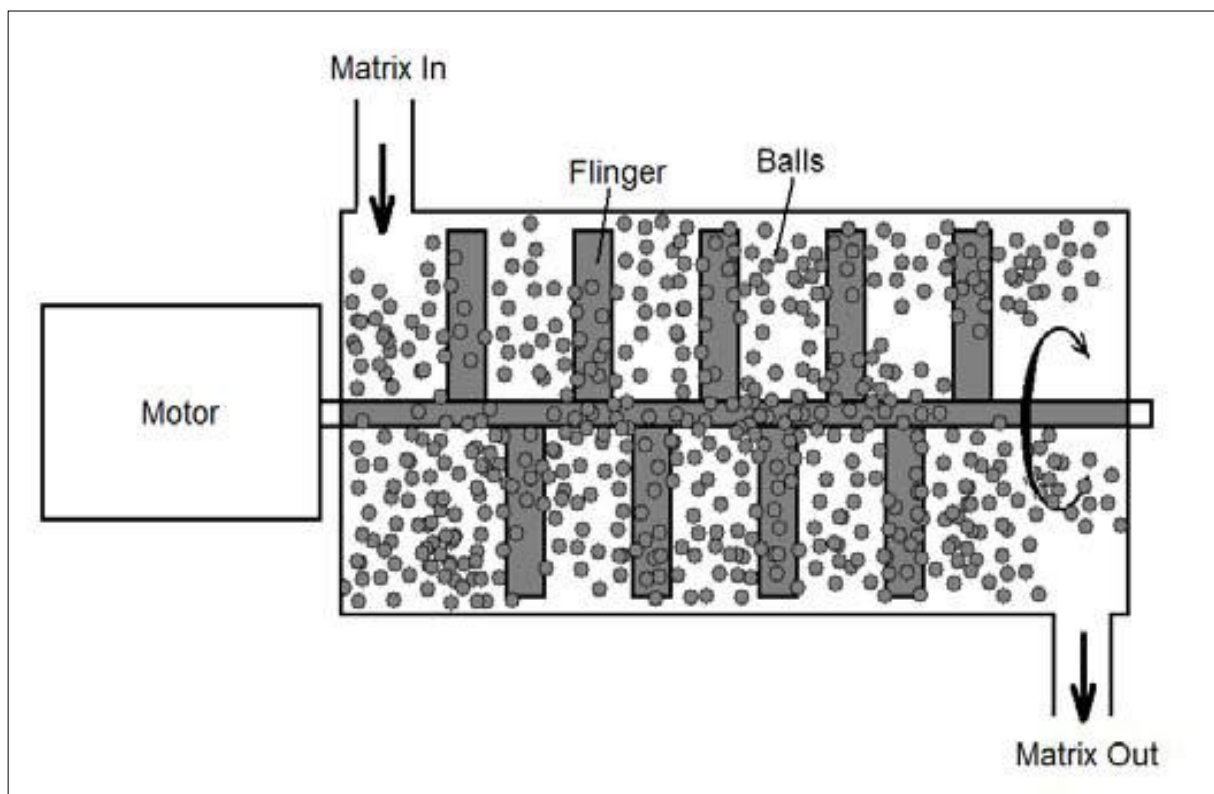
Figure 3.1 – Diagram of a mill (Robertson 2008).

3.1 Mechanochemistry: A Sub-branch of Chemistry

As mentioned in the introductory section of mechanochemistry, it is defined as a branch of chemistry which is concerned with chemical and physico-chemical changes of substances of all states of aggregation due to the influence of mechanical energy. This definition is based on the theoretical scrutiny of Ostwald, a Nobel Prize recipient in 1909, concerning the relationship between chemical and mechanical energies (Heineke 1984. It was Ostwald (fig. 15) himself that coined the name "Mechanochemistry" to describe mechanically initiated reactions in his early works from 1987 to 1909. During the early 1920s,

further developments in the field of mechanochemistry were observed. One of the developments was the invention of the colloidal mill (fig. 3.2) which used principles of mechanochemistry to reduce the particle size of a solid in suspension in a liquid, or to reduce the droplet size of a liquid suspended in another liquid.
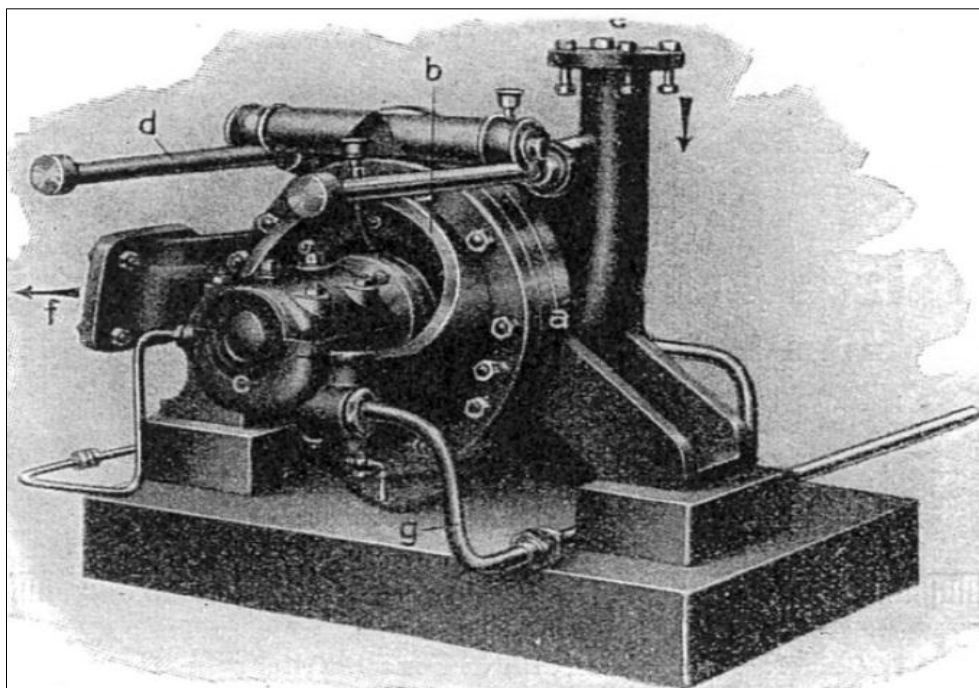
Figure 3.2 – Colloid Mill, Paulson-Oderberg wet mill (Ostwald 1927).

More literature on mechanochemistry were published like "Mechanochemistry and the colloid mill including the practical applications of fine dispersion", a book published in 1928 by Pierce Mason Travis. The author at the time defined mechanochemistry as "the new science of mechanical dispersion involving the use of principles in physical chemistry".

He hesitated to name this science because of his remark "we shall call it mechanochemistry for lack of a better name, as it involves dispersion or defflocculation by mechanical means, thereby bringing about so-called colloidal dispersions" (Balaz 2008).

Mechanochemical reactions were thought to be triggered only by the heat energy created on impact. However, this was dispelled as studies into mechanisms and kinetics of mechanochemical processes were carried out. In saying that, some mechanochemical reactions do fit the model of being initiated by the heat generated from impact.

A study by Urakaev et al. developed a "hot spot" model due to their discovery that temperatures greater than 1,000K occur for fractions of seconds due to friction generated from impact (Urakaev, 2000).

Other mechanochemical triggers have been determined such as the altering of the vibration frequencies of crystal lattices (phonons) to an extent which can disrupt chemical bonds (Tkacova, 1993).

These and more theories and models will be discussed in greater detail in upcoming sections.

3.2 History of Mechanochemistry

The simplest and most widely recognised mechanochemical reaction is the striking of two stones together to make a fire. There is evidence of widespread control of fire by early humans which dates to as far as 128,000 years ago and even further (James 1989). There is even earlier evidence for the controlled use of fire by Homo erectus beginning approximately 400,000 years ago (Gowlett 1984).

The earliest definitive evidence of control of fire by a member of Homo was found in near Lake Baringo in Chesowanja, Kenya. At the site Sediments of a hearth-like collection of stones is associated with lumps of burnt clay. These sediments are dated over 1.4 million ± 70,000 years old (Gowlett 1984).

One of the earliest scientific uses of mechanochemistry closer to modern time was recorded in ancient Greece by Theophrastus of Eresus (fig. 15). He was a student of Aristotle and was his successor as the head of the Lyceum in Athens from 322 B.C to his death in 286 B.C. (Takacs 2000). Theophrastus wrote a book titled "De Lapidibus" which translates to "On Stones"; it is widely recognised to be the oldest books on minerals. The book was translated into English by Sir John Hill in 1774 and an excerpt from book reads "native cinnabar was rubbed with vinegar in a copper mortar with a copper pestle yielding the liquid metal"; the excerpt is describing a mechanochemical process (Takacs 2000). Chemically speaking, the mechanochemical process followed this reaction:

$$HgS + Cu \rightarrow Hg + CuS \qquad \text{Equation 4}$$

The use of vinegar must have been done to counteract the oxidative effects of oxygen in atmosphere.

The late 1st century Roman architect and engineer Marcus Vitruvius Pollio also wrote about the production of quicksilver from cinnabar (Morgan 1914). He wrote about an incident of quicksilver extraction from cinnabar (HgS) when it was being mined that was very different to that reported by Theophrastus.

The excerpt from his book read "During the digging it sheds, under the blows of the tools, tear after tear of quicksilver (metallic Hg)." This too is another early record of mechanochemical reactions. In the early 2nd century, the Roman author and naturalist Gaius Plinius Secundus who was better known as Pliny the Elder also describes the extraction of quicksilver from cinnabar. The method he describes very closely resembles that of Theophrastus and was probably directly copied from his work. Pliny the elder also described a distillation method

of extracting quicksilver from cinnabar as follows "The cinnabar is heated in an iron shell, decomposes and the resulting quicksilver condenses onto a convex lid. The product is collected by wiping it off from the lid." (Goldwater 1972). During the Middle Ages, the mechanochemical preparation of mercury from cinnabar was completely forgotten. By the mid-16th century, a German scientist named Georgius Agricola wrote comprehensive and exhaustive descriptions on metallurgy and mining techniques in his book titled "De Re Metallica" (fig. 3.3).
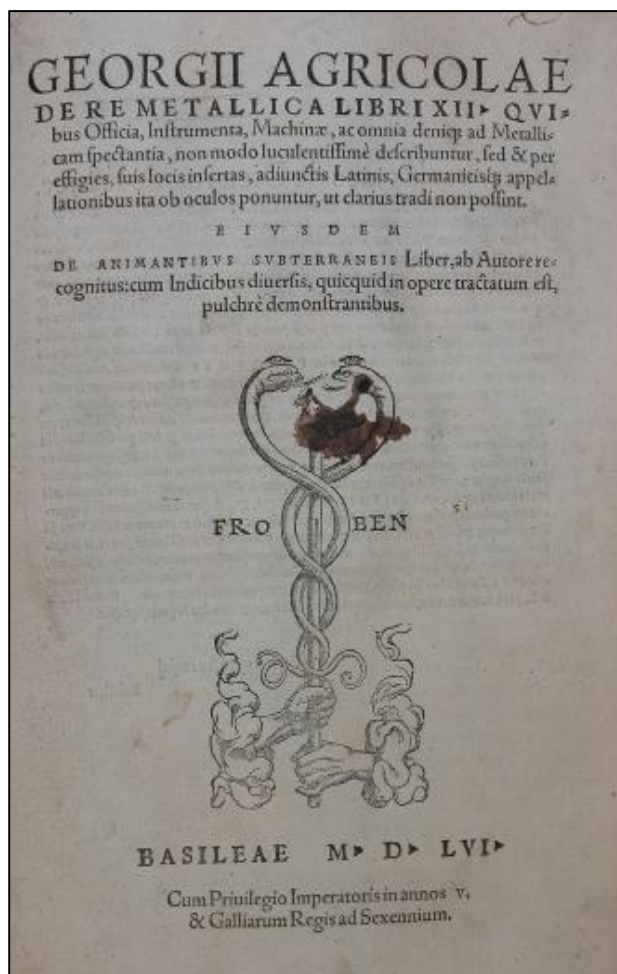
Figure 3.3 – Front cover of De Re Metallica (Courtesy of Wikipedia)

Agricola writes about "the artificial minimum the painters call cinnabaris. This material, when pulverised, sparkles as though it had been adulterated with mercury." He also mentions grinding with a chemical in relation to the preparation of "artificial chrysocolla. The fine mineral is macerated with vinegar until it becomes soft. It is again ground in a mortar and then washed in shells and dried."

Although these processes do represent chemical effects of mechanical action, they are inferior examples compared to the preparation of mercury as described by Theophrastus (Takacs 2000).

In the 17th century, Francis Bacon referred to some procedures to prepare active solids; one of these procedures is milling (Balaz 2008).

During the early 19th century, the famous British scientist Michael Faraday contributed to mechanochemistry. In 1820 he published a direct reference to a mechanochemical process that highlighted the decomposition of silver chloride (Balaz 2008). The decomposition of silver chloride follows the following reaction:

$$2AgCl + Zn \rightarrow 2Ag + ZnCl_2 \qquad \text{Equation 5}$$
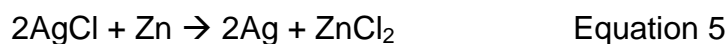
This experiment was carried by mortar milling of the silver chloride and zinc, and according to Faraday the reaction is highly exothermic. This description raises the possibility that of a mechanochemically induced self-sustaining reaction (Takacs 2002). Faraday published a book in 1827 and included a whole chapter on comminution and mortars and then in 1837 he noted that certain hydrated salts dehydrated spontaneously when mechanically treated.

Furthermore, a study conducted by Takacs in 2007 to verify Faraday's decomposition of silver chloride (equation 5) verified the mechanically induced self-sustainability of the process (Takacs 2007).

In the late 19th century, an American chemist named Mathew Carey Lea published articles on the effect of mechanical energy on properties of substances (Lea 1891 a, b, 1823, 1893, and 1894). Lea had introduced new ideas and one of his more ground-breaking papers was on colloidal silver (Lea

1891 a, b). During his work from 1891 to 1894, he discovered three different forms of silver. He described them as allotropic forms of silver and named them "soluble silver, insoluble silver and copper-coloured silver". Lea moved onto to studying the halides of various other metals and one of the most citied results of his work on halides is the disassociation of silver chloride via the application of heat alone and then by introducing mechanical force. When silver chloride was heated, it melted without any decomposition, but when mechanical force was applied to it decomposed into elemental silver and chlorine:

$$2AgCl \rightarrow 2Ag + Cl_2 \qquad \text{Equation 6}$$

This is the first known demonstration of a mechanochemical reaction which yielded different products from that yielded by temperature alone. Lea was the first demonstrate the parallels between light, heat electricity and mechanical force on chemical reactions.

Further developments in mechanochemistry took place in the early 20th century by a Russian scientist named Flavickij and an American chemist named Leslie Henry Parker. Flavickij published pioneering articles on solid state reactivity via reactive milling in 1903 and 1909.

Parker continued the work done by Lea and expanded on it. He realised that Lea research revolved around the mechanochemistry of single compounds (Parker 1914) so he researched double compound reactions by reactive milling. Parker designed the first mechanochemical reactor to study the effect of reactive milling of more than one compound (fig. 3.4) (Parker 1914). He milled sodium carbonate and barium sulphate in his mill and discovered that sodium carbonate transformed very slightly into sodium sulfate:
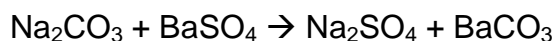
$$Na_2CO_3 + BaSO_4 \rightarrow Na_2SO_4 + BaCO_3 \qquad \text{Equation 7}$$

He would later discover that under ambient temperatures, he could greatly increase the interaction of two solids via mechanical stimulation if he would increase the speed of the mill i.e. increase the mechanical force (Parker 1918). Both Parker and Lea wrote about the importance of controlling the atmosphere during the milling process as touched upon by Theophrastus nearly 2,200 years ago (Balaz 2008).

A – Mortar
B – Iron Collar
C – Pestle
D – Handle
E – Rubber Tubing
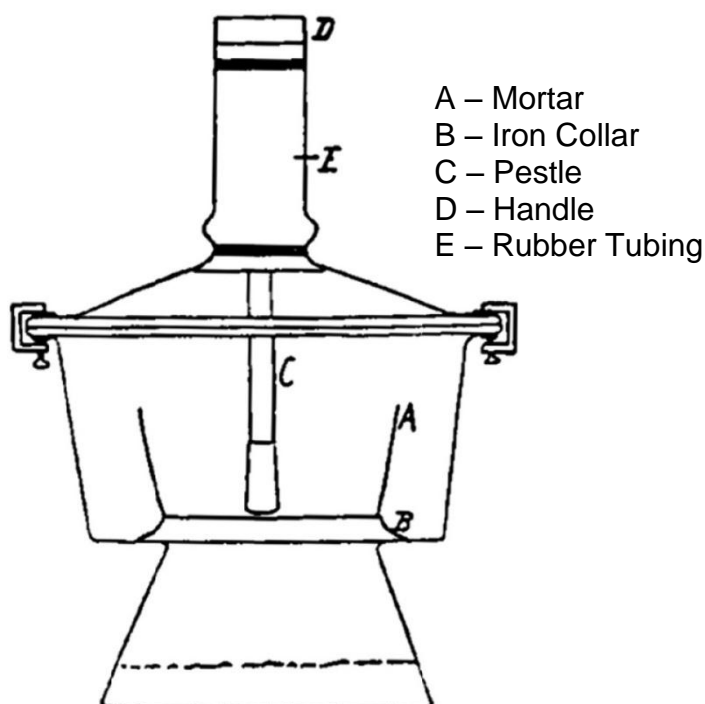
Figure 3.4 - The first mechanochemical reactor designed and built by Parker (Parker 1914)

After the published works of both Flavickij and Lea, a German scientist named Tamman studied the effect of mechanical energy on metals and published his finding in 1929. He determined that during the milling the process, that the majority of the energy was transferred to heat and a small amount, about 10%, is retained within the metal.

This energy is stored as potential energy which increases the thermodynamic potential of the metal which allows for increased dissolution velocity (Tamman 1929.)

Also in the 1920's the mechanochemical effects on organic molecules were first elucidated mainly by German scientist Wanetig. The work on the mechanochemistry of organics was indirectly initiated by the paper industry (Balaz 2008).

After the works published during the 1920's, there was a period of inactivity within the academic field of mechanochemistry. This gap was from the 1920's to around the late 1940's/early 1950's.

Further development on the mechanochemistry of organic molecules was re-established around in the late 1950's. Some of the work of that time period looked at the mechanical degradation of polymers. It was determined that the reactivity of polymers is parallel their molecular weights are inversely proportional. In other words, if the reactivity of a polymer increases, its molecular mass decreases.

 In the following decades leading to the turn of the 21st century, many more studies investigated various avenues of mechanochemistry. Articles on decomposition of solids, oxidation reactions, effects of friction and rolling were published.

One particularly interesting book published in 1958 by Bowden and Tabor described temperatures as high as 700°C were recorded at the point of contact between solids subjected to friction (Bowden 1958). This study launched the "Hot Spot" theory of mechanical initiation of chemical reactions.

3.3 Theories and Models of Mechanochemistry

The initiation of chemical reactions by mechanical forces has been studied by many scientists over the years. There a lot of theories and models describing how an impact or friction brings about a chemical change to a molecule.

Mechanochemical reactions were thought to be triggered only by the heat energy created on impact. However, this was dispelled as studies into mechanisms and kinetics of mechanochemical processes were carried out. In saying that, some mechanochemical reactions do fit the model of being initiated by the heat generated from impact. Other mechanochemical triggers have been determined such as the altering of the vibration frequencies of crystal lattices to an extent which can disrupt chemical bonds (Tkacova, 1990).

The following few sections will highlight only a few of the main theories and models which initiate chemical reaction by mechanical and tribological stimulation.

3.3.1 Direct Bond Breaking by Impaction

Within a reactive mill (fig. 11), organic molecules are subjected to a high number of impacts by the ball bearings. As the mill's motor spins, it spins the axle and flangers which crash into the ball bearings and accelerates them to speeds of around 10ms^{-1}. As the ball bearing travel at these high speeds, they would crash into the organic molecules. These impacts start to stress the bonds between the atoms of a molecule and eventually break. The breakage of these bonds will yield high energy radicals and ions. Even the matrix in which the organic molecules inhabit will also undergo the same process of stressing of the bonds and eventual breakage (fig. 3.5).
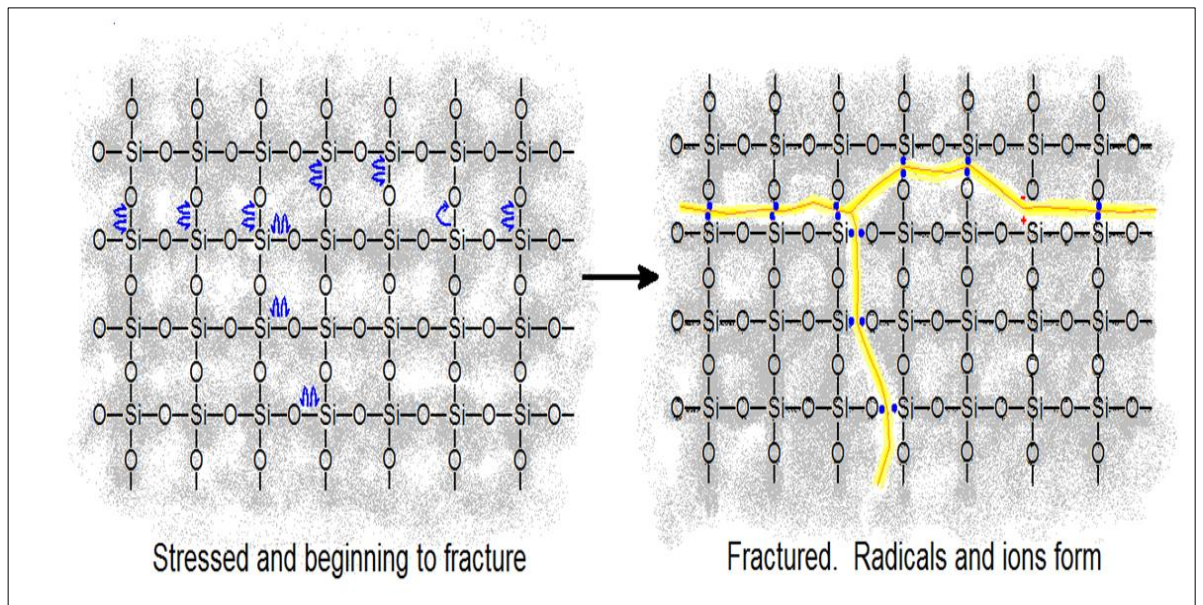
Figure 3.5 - The breaking of SI-O bonds in quartz (Robertson 2008)

Figure 16 depicts the stress of the quartz bonds between silicon and oxygen. This is an example of sand contaminated with organic contaminants being milled with ball bearings to destroy the contaminants. Once the silicon and oxygen bonds are broken, a surface rich with reactive sites is exposed to the constituents of the mill's atmosphere, which includes the targeted organic contaminants (fig. 3.6).
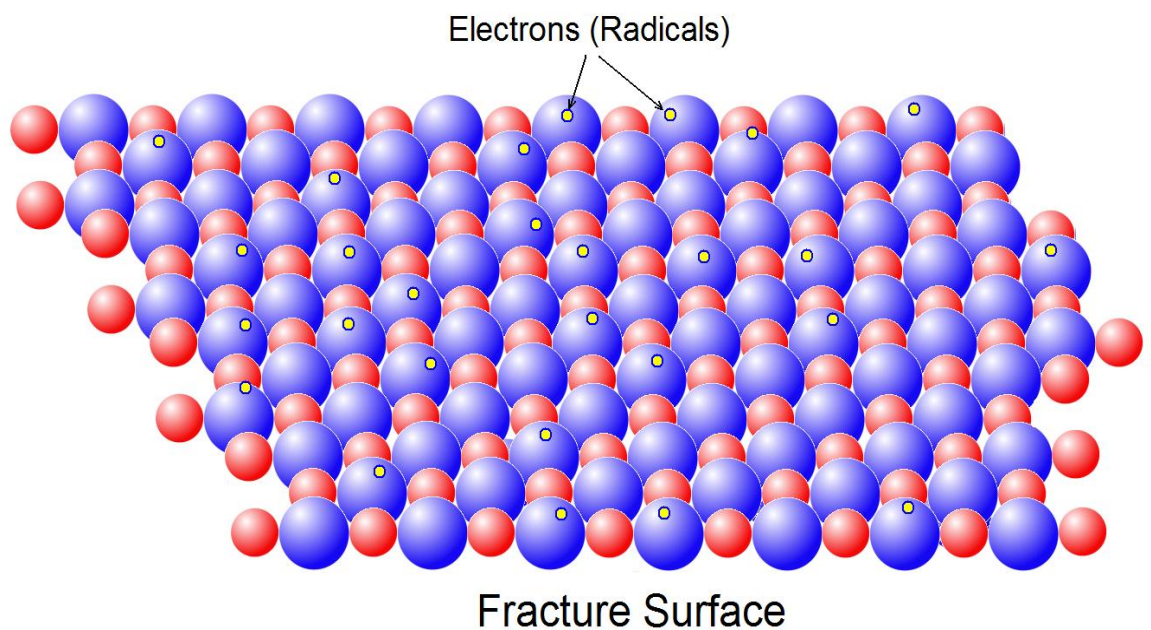
Figure 3.6 – Fractured surface with many reactive sites (Robertson 2008).

During the milling of quartz, Si-O bonds are broken and radicals are created (Hasegawa 1995; Steineke 1987). Approximately 5 x 1018 Si-O bonds are broken per m^2 increase in surface area while the number of E' centre (≡Si•) and non-bridging oxygen hole centre (NBOHC) (≡Si-O•) radicals formed is approximately 1 x 1018 per m^2 of each (Heineke 1984). The homolytic cleavage of Si-O bonds in quartz during milling is shown in Equation 7 while the heterolytic cleavage is shown in Equation 8 (Bellingham 2005).

$$≡Si – O – Si≡ → ≡Si• + •O-Si≡ \qquad \text{Equation 7}$$

$$≡Si – O – Si≡ → ≡Si+ + -O-Si≡ \qquad \text{Equation 8}$$
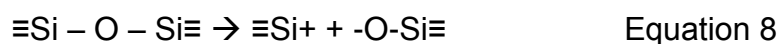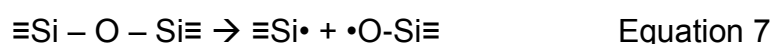
The organic molecules would then settle on the surface and react with the exposed reactive sites. Electrons are transferred forming energetic ions and radicals, these then fragment to form smaller daughter ions, radicals and neutral species (fig. 3.7).
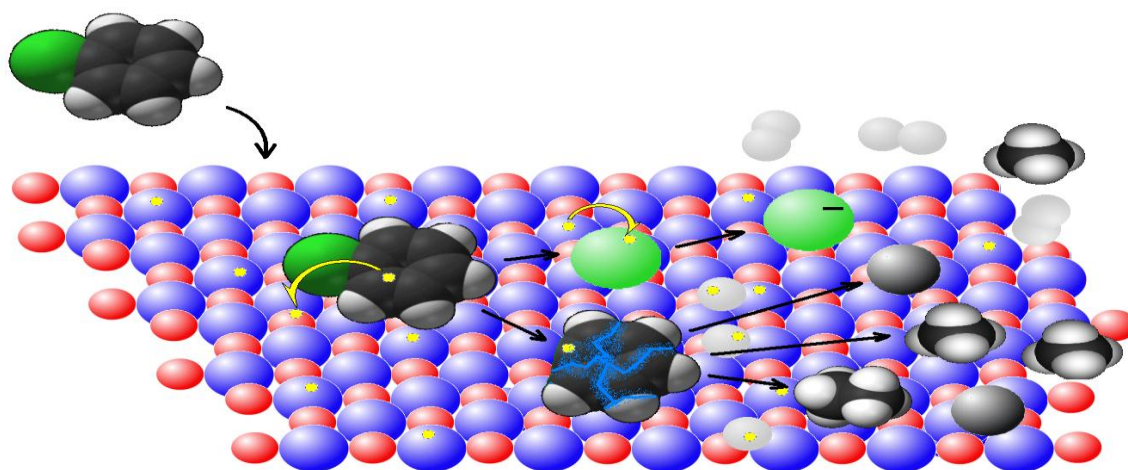
Figure 3.7 – Reactions on the fragmented reactive surface (Robertson 2008).

The kinetics of this type of activation model is simple for the majority of the reaction. They are first order in substrate therefore:

$$[Substrate] = Ae^{-kt} \qquad \text{Equation 9}$$

Due to the nature of its reaction kinetics, the reactions can be described by the concept of half-life (fig. 3.8).
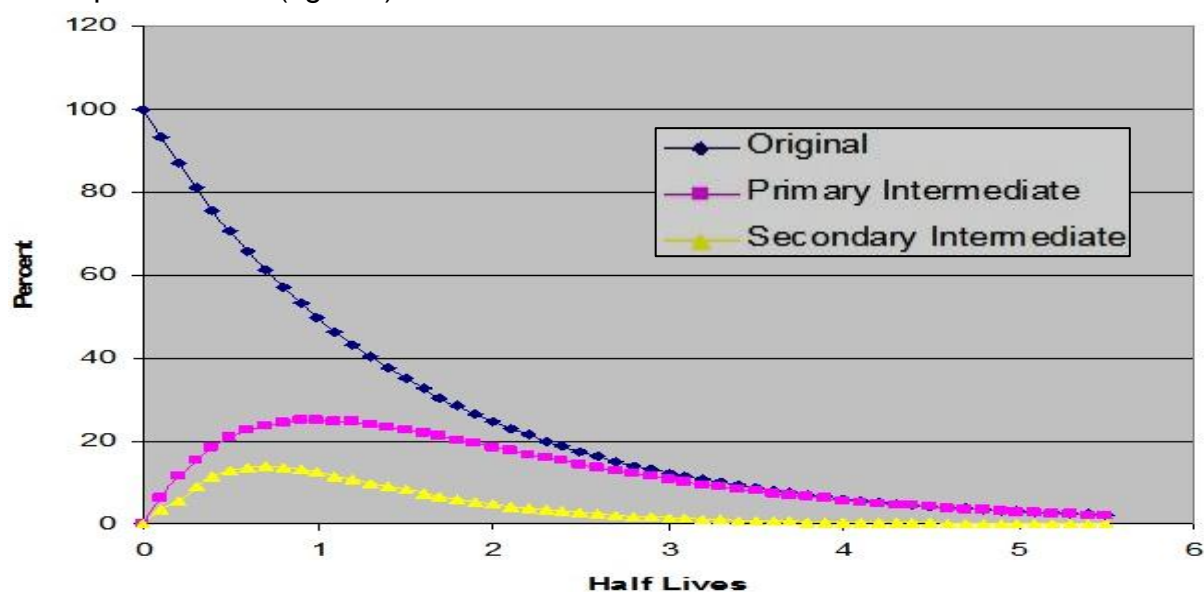
Figure 3.8 – Destruction of organic molecule as percentage of original amount (Robertson 2008).

3.3.2 Hot Spot Theory

The Hot Spot theory was one of the first proposed models of mechanically initiated chemical reactions. The model was developed by Bowden, Tabor and Yoffe between 1952 – 1958. In their studies, they discovered that during the friction between two solids temperatures are generated that can reach up to $700°C$ for duration of about $10^{-4} – 10^{-3}$ seconds on surface areas of about $1\mu m^2$ (Bowden and Yoffe 1952, 1958; Bowden and Tabor 1958).

Therefore the rational of the hot spot theory is that the high temperatures causes stress on the bonds of organic molecules which eventually break them hence initiating the reaction. There has been on-going debate about the high temperatures generated during friction and points of impact. Continuing experiments are still being carried today to expand on the theory. Some of

these experiments looked at the temperatures generated during the propagation of a crack (Weichert 1974) while other studies looked at extremely localised areas where these temperature spikes are generated. An example of such an experiment looked at bubbles created by cavitation which are flooded following the absorption of ultrasound in liquids (Suslick 1990; Butyagin 1994). Another study by Weichert in 1976 looked to investigate these localised and specific occurrences by recording temperatures generated by a propagating crack. He proved that high temperatures were generated at the tip of propagating crack in three different solids listed below:

Table 3.1 – Maximum temperatures the tip of the propagating crack (Weichert 1976)

Material	Glass	Quartz	Sugar
Temperature ($^\circ$C)	*2927*	*4427*	*2227*

3.3.3 The Magma-Plasma Model

The Magma-Plasma (MP) model was first proposed by a trio of German chemists named Thiessen, Meyer and Heinicke in 1967. This model describes the initiating mechanism of a mechanochemical reaction between two colliding solids.

The MP model is a good candidate in explaining mechanochemical reactions within a ball mill. The model suggests that a large amount of energy is liberated at the point of impact of two solids.

This bubble of energy generates triboplasma (fig. 3.8) which emit short-lived but highly energetic electrons, photons and radicals (Thiessen 1967).
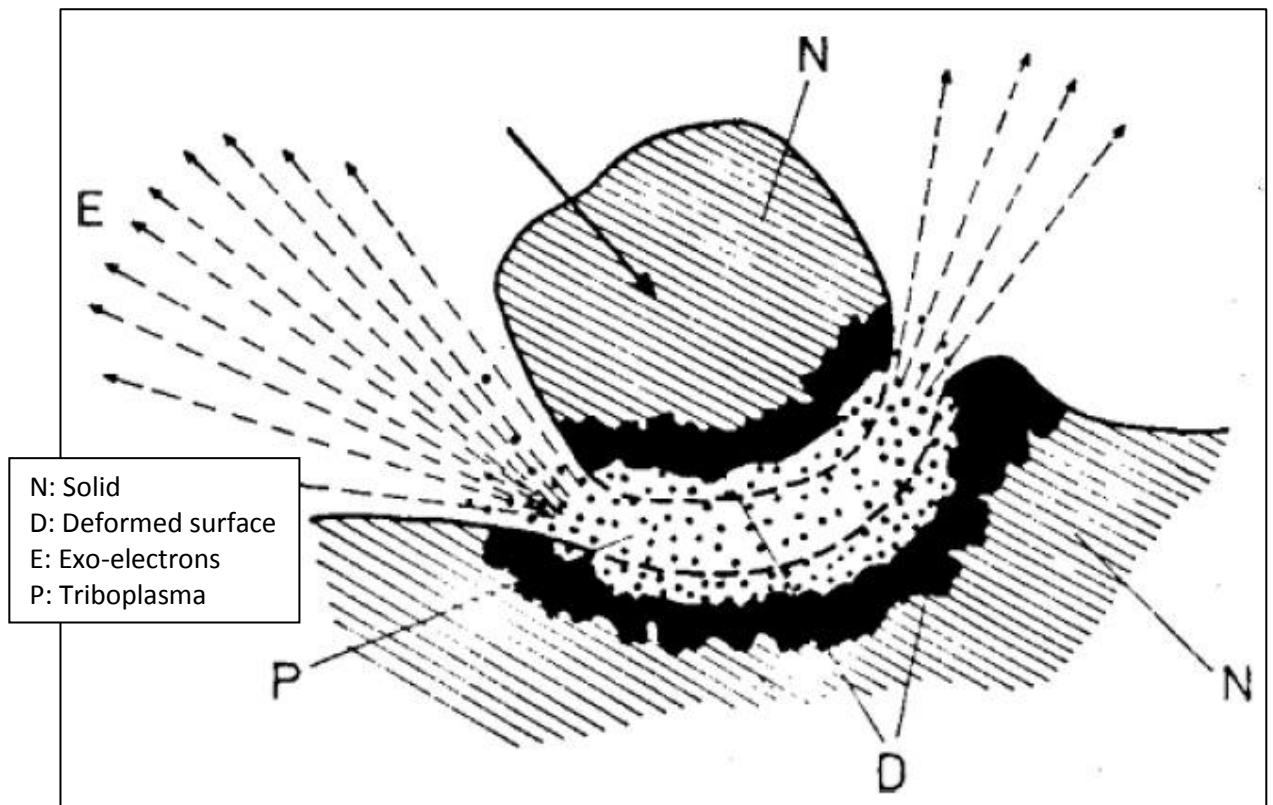
Figure – 3.8 Magma-Plasma Model (Kajdas 1994)

Temperatures reaching 9727°C (Theissen 1967) and different reactions were identified and distinguished. Reactions occurring within the triboplasma were initiated differently than the reactions taking place at the highly excited surfaces of particles. This meant that at the point of impact of two solids creates conditions to allow mechanochemical reactions to take place, but there are many different initiating mechanisms that drive these reactions i.e. there is no single governing mechanism. Efforts were made to further understand the various and complex mechanisms that occur in the MP model.

To better understand the sequence of events that occur at impaction, a German chemist named Heinicke suggested a hierarchy of energetic states induced by mechanical forces that can initiate mechanochemical reactions. He organised the hierarchal model (table 3.2) of energetic states by the level of excitation states and temporal occurrence. Therefore the most highly excited states

having the shortest excitation times are listed first and the numerous other states with smaller excitation are listed according to their temporal occurrence in the dissipation phase into the model (Heinicke 1984).

Table 3.2 – Lifetimes of excitation processes in mechanically activated solid

Excitation Process	Relaxation Time
Impaction	$> 10^{-6}$ s
Triboplasma	$< 10^{-7}$ s
Gaseous Discharge	$\sim 10^{-7}$ s
Hot Spots	$10^{-3} - 10^{-4}$ s
Electrostatic Charging	$10^{-2} - 10^{5}$ s
Exo-electron Emissions	$10^{-6} - 10^{5}$ s
Triboluminescence	$10^{-7} - 10^{3}$ s
Lattice Defects	$10^{-7} - 10^{6}$ s
Dislocation Motion	10^{5} cms^{-1}
Lattice Vibrations	$10^{-9} - 10^{-10}$ s
Fracture Formation	$10 - 10^{3}$ cms^{-1}

More recent studies into the MP model have further distinguished the mechanochemical reactions occurring at impaction. Nakayama et al. have determined that the origins of chemical reactions in mechanical contacts are threefold depending on the reaction regions: inside the contact area (ICA), near or in the vicinity of the contact area (NCA) (especially in the gap between a sphere and a plan), and far outside the operating contact area (OCA) (Nakayama 2006). Therefore, the energies responsible for initiating mechanochemical reactions do not only occur in temporal sequence, but also my location relative to the point of friction and impact (fig. 3.9).
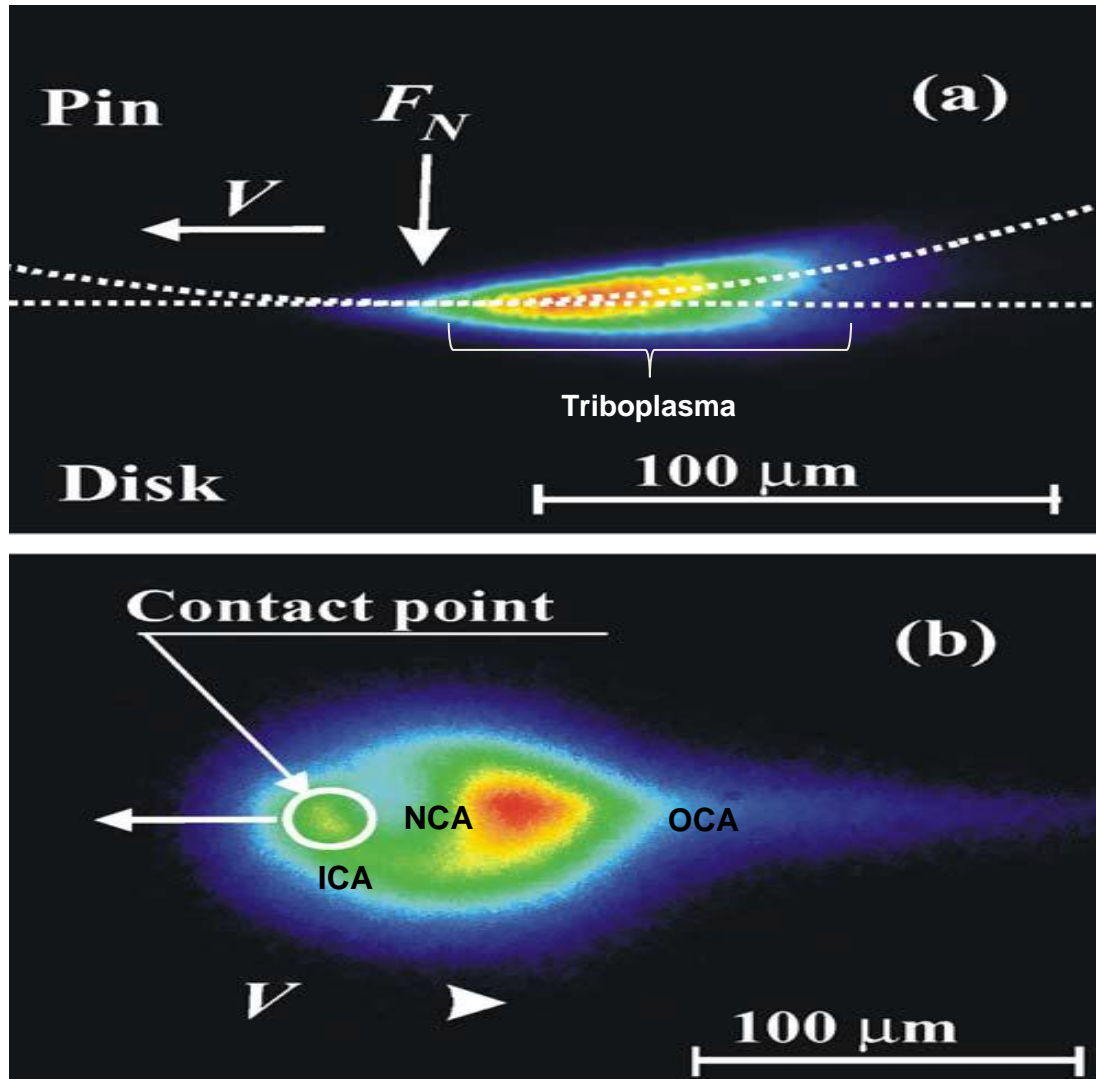
Figure 3.9 - Side (a) and plane (b) view images of triboplasma and reaction regions (Nakayama 2006).

3.3.4 Phonon Dislocation Theory

Proponents of dislocation theory say that when a mechanical force is applied onto a solid, dislocations within the structure of that solid occurs. These weakened areas subsequently become increasingly chemically active (Gutman 1974).

As a direct result of these dislocations, phonons are produced due to the interactions between the multiple dislocations within the solid (fig.3.10).

The phonon theory highlights the resultant phonons' effects, distribution and origins in the context of the disordering of the solid (Bertenev 1969).

A more recent study also looked at the disruption of bonds within molecules by the release of phonons. Tkacova et al. also determined that altering of the vibration frequencies of crystal lattices (phonons) in a ball mill to a certain extent can disrupt chemical bonds and degrade the target molecules (Tkacova, 1990).
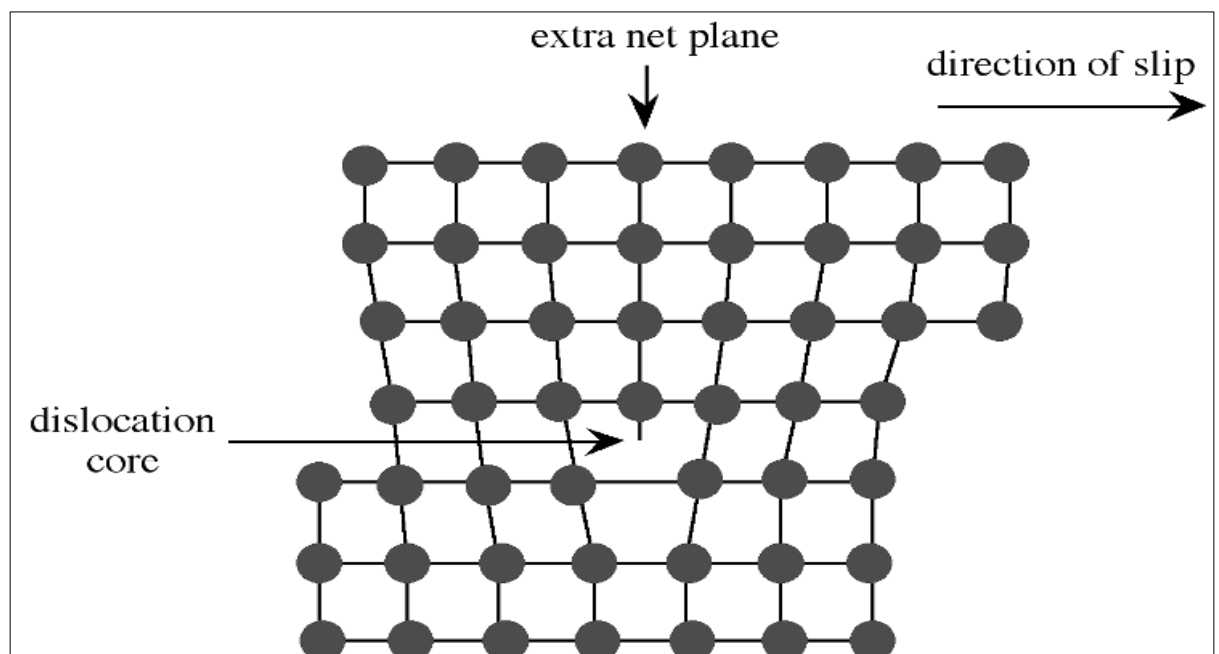
Figure 3.10 – Simplified diagrammatic representation of dislocation within a lattice (Courtesy of cnx.org)

Chapter 4 - Contaminated Land Remediation by Ball Milling

The study of the mechanisms of mechanochemistry is being continuingly elucidated since the first recorded scientific experiment recorded by Theophrastus over 2,200 years ago. The principles of mechanochemistry have various applications, e.g. mechanical alloying, paint pigments, ceramics and pharmacology.

Only in recent times the mechanochemistry of ball milling has been used to tackle land contaminated by both organic and inorganic contaminants. The same theories and models that propagate chemical reactions in mechanochemistry are used to degrade and alter the contaminant molecules. As mentioned in section 3.3.1, this mechanical force is produced by the balls which crash into the soil and contaminants at velocities of around 10 ms^{-1}. This impact energy initiates chemical reactions in both the soil and target contaminants by the mechanism described in section 3.3 Theories and Models in Mechanochemistry.

These mechano-mechanisms initiate certain specific reactions that alter the chemical structures of organic pollutants. Some of the reactions induced by these mechano-mechanisms are mechano-degradation, mechano-dehalogination, mechano-dechloronation and mechano-polymerisation.

These reactions are further discussed below in relation to common organic pollutants found in soils all over the world and how these organic pollutants are structurally altered and rendered harmless.

4.1 Mechanochemical Reactions

4.1.1 Mechanochemical Dehalogenation

Mechanochemical dehalogenation is proving to be very successful in remediating chlorinated contaminants such as PCDDs, PCDFs, PCBs and PVC waste. To achieve the mechanochemical dehalogenation of contaminants within a soil sample, it must be mechanically activated in a ball mill with a strong reducing agent. Birke et al. demonstrated that "Dehalogenation by Mechanochemical Reaction" (DMCR) is a fast and highly effective method of remediating soils contaminated by polyhalogenated pollutants (Birke 2004). In their experiment, they utilised a ball mill to initiate the reductive dehalogenation of PCBs and PCP to their parent hydrocarbons in high yields, biphenyl and phenol respectively. An example of reductive dehalogenation is that of milling a soil sample contaminated by a PCB with base metal magnesium as the reducing agent. As the contaminated soil is milled, hydrogen is liberated which allows the magnesium to reduce the PCB which breaks off the chlorine bond (dechlorination) producing magnesium chloride salt as follows:

$$R\text{-}Cl + Mg + H \rightarrow R\text{-}H + MgCl_2 \qquad \text{Equation 10}$$

Highly toxic reactants $\rightarrow$ None toxic products

Many other studies have also looked at and successfully demonstrated that dehalogenation and mainly dechlorination (due to polychlorinated molecules being the leading class of toxic pesticides contaminating soils) is an effective method of remediating land contaminated by halogenated pollutants (Yasumitsu 2003; Birke 2004; Tongkamp 2008). Pizzigallo et al. also looked dehalogenation in terms of mechanochemical removal of organo-chlorinated compounds by

inorganic component of the soil. They examined the catalytic efficiency of two metal oxides, ferrihydrite and birnessite and of a ferruginous smectite, towards organic molecules such as 4-chloroaniline (4-CA), pentachlorophenol (PCP), and five polychlorinated biphenyls (PCBs) characterised by different number and position of chlorine atoms (Pizzigallo 2004). A comparison of the destructive efficiencies of mechanochemical dechlorination and batch experiment for PCP and 4-chloroaniline was done. The removal of 4-CA and PCP by the mechanochemical procedure resulted more effective than by batch contact in the presence of birnessite and ferrihydrite, particularly at higher pH (100% removal of 4-CA by birnessite in 30 min at pH 8.6 after the mechanochemical contact compared to 20% removal using the batch interaction at the same pH) (Pizzigallo 2004).The mechanochemical contact of PCBs and birnessite produced a removal of pollutant that was a function of the number of chlorine atoms (complete removal of 2,2'-dichlorobiphenyl in 10 days and a removal of 30% and 20% of 2',3,4-trichlorobiphenyl and 3,3',4,4'-tetrachlorobiphenyl, respectively in 90 days) and of the position of chlorine atoms about the biphenyl rings (100% of 2,2' dichlorobiphenyl in 10 days, 84% of 3,3'-dichlorobiphenyl in 15 days and 40% of 4,4'-dichlorobiphenyl in 27 days) (Pizzigallo 2004).
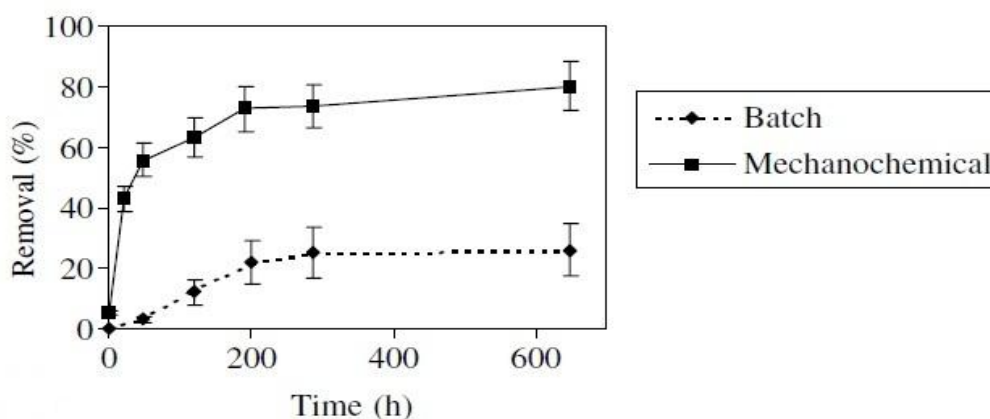
Figure 4.1 – Removal of pentachlorophenol by mechanochemical and batch procedures. (Pizzigallo 2004)

4.1.2 Mechanochemical Degradation

Mechanochemical degradation occurs when large amounts of mechano-energy are applied onto molecules. The bonds holding the molecules together become stressed via the various mechanochemical models discussed in section 3.3.

Field et. al. have carried out a number of investigations in biphenyl, naphthalene, anthracene and phenanthrene in mechanochemistry. They have discovered that with apparently non-reactive matrices (alumina and silica), aromatic hydrocarbons treated mechanically were destroyed and converted to carbon (as graphite) and a variety of partly hydrogenated materials. They also discovered that silica is more effective medium in the destruction of organic material compared with alumina but oxygen slows down the rate of reactions (Field 1997).

Degradation of organic molecules occurs during the late stages of ball milling. In the early stages, mechanochemical dehalogenation takes place as this step does not require significant amount of mechanical or thermal energy. This is true because reduction reactions of early stage dehalogenation do not require high energies therefore occur quickly, usually after only 30 minutes of milling (Pizzigallo 2004).

Mechanochemical degradation occurs in later stages of milling because it requires a large amount of mechanical energy. As the energies that are being applied onto the molecules within a ball mill increases, direct bond breaking start to occur, as well as structural alterations, due to the action of triboplasma and phonon induced dislocations (Bertenev 1969; Gutman 1974; Tkacova 1990).

Furthermore, as impaction and frictions between the ball bearing and the interior surface of the mill continue, a large amount of heat is generated. This heat is able to initiate spontaneous burning reactions in highly exothermic systems involving chloroorganic during milling.

Monagheddu et al. studied the reduction of PCDDs and PCDFs in contaminated muds by mechanically induced combustion reactions. They determined that it is possible to degrade difficult contaminants like PCDDs and PCDFs under combustive regimes when mixed with a primer mixture such as hexachlorobenzene and calcium hydride and that the contaminants are burnt by the heat produced by the principal reactants (Monagheddu 1999). This mechano-incineration has an advantage over traditional incineration methods because the high temperatures and extreme chemical reactivity levels can be achieved under carefully controlled conditions (Monagheddu 1999). Similar studies like this have also reached similar conclusion that ball milling dioxin-based molecules is an effective non-combustive technology for dioxin degradation that does not produce organochlorine compounds as reaction products (Cao 1999; Nomura 2005; Caschili 2006).

4.1.3 Mechanochemical Polymerisation

Polymerisation is a chemical process leading to the formation of macromolecules that consist of repeating structural units (Wooff 2000). In other words, it is the reacting of monomer molecules together in a chemical reaction to form polymer chains, i.e. Monomers bonded in series. Mechanochemical polymerisation is a process where mechanical energy is directly responsible initiating a polymerisation reaction. Logically, one would imagine that a high energy ball mill applying large amount of mechanical energies on any polymer

or macromolecule would result in its shortening and eventual complete degradation into small inert species; this is true for the most part. According to several scientists studying mechanochemical reactions (Heineke 1984; Kaptan 1997; Shmidt-Naake 2001) when a macromolecule or polymer is placed under mechanical stress (ball milling), the average length of the polymer chains is reduced. This chain shortening occurs when milled with or without the presence of an inorganic matrix. The cause of the chain shortening is due to the homolysis of the covalent bonds holding the polymer together e.g. C-C bond.

Interestingly, the opposite is also true, however to a small extent. If monomers are milled alone or in the presence of an inorganic matrix, they will polymerise (Hasegawa 2001). The process of mechano-polymerisation occurs during milling by the formation of ions and high energy radicals. These high energy species initiate bonding between the monomers to form polymers.
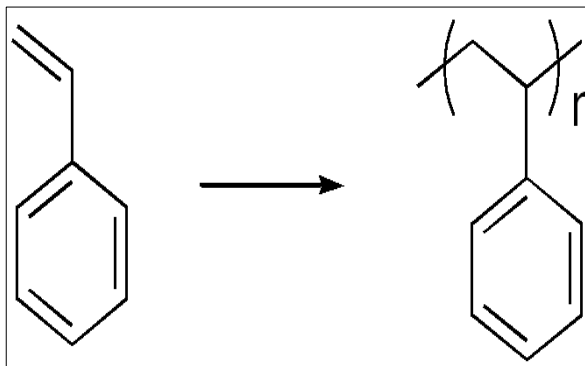
Figure 4.2 - Alkene polymerisation example of styrene losing its double bond to bond with another styrene molecule. (Courtesy of Wikipedia)

4.2 Ball Mill Reactors

This study utilised a ball mill to impart the mechanical force required to initiate the mechanochemical reactions to test hypothesis on mechanochemical remediation of organic pollutants. Ball milling is used for a wide varieties of reasons and industries e.g. paint pigment, ceramics, pharmacology, coatings and alloying. This wide variety of uses is also reflected by the wide variety and types of ball mills.

4.2.1 Planetary Ball Mill

As the name suggests, in a planetary ball mill the grinding jar rotates about its own axis and in the opposite direction around the common axis of the "sun" wheel. This produces grinding ball movements with high pulverising energy. The combination of impact and frictional forces results in a high degree of pulverisation (fig. 4.3).
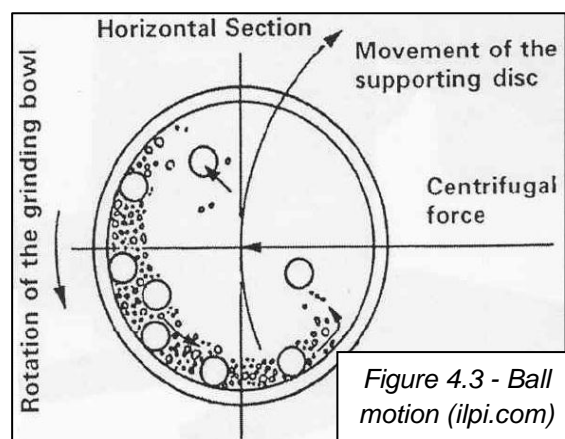
Figure 4.3 - Ball motion (ilpi.com)

As the grinding jar rotates about its own axis, the balls gain centripetal force. This causes the balls to travel across the inner -wall of the grinding jar and impacts friction on the inner-wall and any substances that is being milled. As the grinding jar rotates along its own axis, it is also simultaneously rotating in the opposite direction around the common axis, this causes the balls to lift off (negate the centripetal force momentarily) the inner-wall of the grinding jar and smash against the opposing inner-wall. This action accounts for the pulverisation action of the planetary ball mill. Due to the double effect of friction

and impaction, planetary ball mills impart large amounts of mechanical energy onto sample.

4.2.2 Shaker/Mixer Mill

The shaker or mixer mill is a very high energy impact mill; more so than the planetary ball mill. The usual shaker/mixer mills are equipped with a single grinding jar where the sample and grinding balls are placed. The grinding jar is then placed horizontally between two metal arms and clamped in place.

This type of mill is very popular for laboratory experiments and is also used for alloy screening processing (Kaupp 2005).

The mode of action of this mill is rapid back and forth movement along a horizontal plane (shaking) coupled with another continuous left to right shaking action; both shaking actions are set at speeds of a few thousand rpm. Therefore, the grinding jar is simultaneously shaken in two directions at very high speeds which impart very high mechanical energy onto the sample via the grinding action of the balls.

Figure 4.4 - A SPEX model shaker/mixer mill. (Courtesy of Direct Industry)

4.2.3 Attritor Mill

The design of an attritor ball mill utilises grinding more than impaction; however impaction does occur often enough to contribute to the total energy output. The grinding jar stands vertically as opposed to horizontally like the shaker mill and an axle or agitator with agitator pegs is lowered into the jar (fig. 4.5).

Figure 4.5 – Attritor mill arrangement. (Courtesy of Ingalls Equipment)

The grinding jar is filled halfway with grinding balls. These balls can be made from a variety of materials and their use is dependent on the media to be ground e.g. carbon steel, stainless steel, chrome steel, tungsten carbide and ceramic balls are some of the commonly used grinding balls. The material to be milled is then added and the jar is sealed. The material and grinding balls are then agitated by the agitator with agitator pegs, rotating at high speed. This causes the grinding balls to exert both shearing and impact forces on the material. The final result of the process is an extremely fine material, measured in microns.

4.2.4 This Study's Ball Mill

For this experiment, a planetary ball mill was chosen. The mill of choice was the Retsch PM100 planetary ball mill (fig. 4.6) manufactured by Retsch Industries in Germany.

Applications	pulverizing, mixing, homogenizing, colloidal milling, mechanical alloying
Field of application	agriculture, biology, chemistry / plastics, construction materials, engineering / electronics, environment / recycling, geology / metallurgy, glass / ceramics, medicine / pharmaceuticals
Feed material	soft, hard, brittle, fibrous - dry or wet
Size reduction principle	impact, friction
Material feed size*	< 10 mm
Final fineness*	< 1 μm, for colloidal grinding < 0.1 μm
Batch size / feed quantity*	max. 1 x 220 ml, max. 2 x 20 ml with stacked grinding jars
No. of grinding stations	1
Speed ratio	1 : -2
Sun wheel speed	100 - 650 min^{-1}
Effective sun wheel diameter	141 mm
Type of grinding jars	"comfort", optional areation covers, safety closure devices
Material of grinding tools	hardened steel, stainless steel, tungsten carbide, agate, sintered aluminium oxide, zirconium oxide
Grinding jar sizes	12 ml / 25 ml / 50 ml / 80 ml / 125 ml / 250 ml / 500 ml
Setting of grinding time	digital, 00:00:01 to 99:59:59
Interval operation	yes, with direction reversal
Interval time	00:00:01 to 99:59:59
Pause time	00:00:01 to 99:59:59
Storable SOPs	10
Measurement of input energy possible	yes
Interface	RS 232 / RS 485
Drive	3-phase asynchronous motor with frequency converter
Drive power	750 W
Electrical supply data	different voltages
Power connection	1-phase
Protection code	IP 30
Power consumption	~ 1250 W (VA)
W x H x D closed	630 x 468 x 415 mm
Net weight	~ 86 kg

Figure 4.6 – Technical details and picture of the Retsch planetary ball mill. (Courtesy of Retsch)

Chapter 5 – Equipment, Materials and Methodology

5.1 Milling of Organic Compounds in Soils

5.1.1 Milling Equipment

5.1.1.1 Mechanochemical Reactors

A Mechanochemical reactor is any device that applies mechanical energy on to a sample. The most common type of mechanochemical reactors are the ball mills; these mills come in many different configurations as described in section 4.3.

The mechanochemical reactor that was used in this study was a Retsch PM100 planetary ball mill (fig. 28). The mill is equipped with a 500 mL chrome steel grinding jar, a 50 mL chrome grinding jar, a 50ml zirconia grinding jar and a variety of chrome steel and zirconia grinding balls.

The grinding jar rotates about its own axis and about the sun wheel (central axis) in the opposite direction i.e. the jar rotates in a clockwise direction while orbiting the sun wheel in a counter-clockwise direction.

This opposing rotational movement allows a superimposing centripetal force to act upon the grinding balls and sample. As a result the grinding balls and sample move alone the grinding jar's interior surface and then is pushed off and smashed into the opposing interior wall due to the Coriolis Effect.

This action allows for the sample to be ground due to the centripetal force and to be pulverised by the impaction due to the Coriolis Effect.

5.1.2 Laboratory Analysis Equipment

5.1.2.1 Gas Chromatograph – Mass Spectrometer

Thermo Trace GC Ultra coupled with a Thermo DSQ unit. The column used was a Varian factor FOUR column, VF-5ms, 30mx0.25mm, 0.25μm. Part no. CP8944. The GC-MS was equipped with a National Institute of Standards and Technology library used to identify intermediates.

5.1.2.2 Atomic Absorbance

A Thermo atomic absorbance machine was used to determine the iron concentrations in milled samples.

5.1.2.3 Ultrasonic Bath

A Filli Cavalin ultrasonic bath from Italy was used for extraction of organic compounds from solid samples into the solvent solution.

5.1.2.4 Centrifuge

Centrifuge (MSE) was used to centrifuge treated samples from the solvent when required.

5.1.2.5 Kiln

A W. D. McGregor Ltd. kiln was used to dry soil sample during the moisture and clay-drying experiments. The kiln has a maximum firing temperature of 1000°C. It was fitted with a Eurotherm temperature control unit.

5.1.2.6 GC Syringe

A Thermo GC syringe was used to inject samples into the GCMS. It has a temperature range of 5-115°C, an accuracy of ±1% and functional pressure of 100psi.

5.1.3 Materials

5.1.3.1 Soil Matrices

5.1.3.1.1 Quartz

Quartz was sourced from a past student's experiment. The former student purchased Mataia silica sand from Sand Resources (NZ) Ltd in Auckland, New Zealand. The silica was observed under a microscope and identified as quartz. The typical chemical analysis, as provided by Sand Resources, is given below:

Table 5.1 – Quartz constituents

Compound	Formula	Concentration (%)
Silica	SiO_2	99.32
Aluminium Oxide	$Al2O_3$	0.16
Calcium Oxide	CaO	0.10
Titanium Oxide	TiO_2	0.10
Ferric Oxide	Fe_2O_3	0.07
Magnesium Oxide	MgO	0.02
Sodium Oxide	Na_2O	0.02
Potassium Oxide	K_2O	0.01
Loss on ignition		0.20
	TOTAL	100

5.1.3.1.2 China Clay

The China clay was sourced from Western Potter Supplies, Auckland, New Zealand. China clay is the colloquial name of kaolinite which is clay mineral with chemical composition $Al_2Si_2O_5(OH)_4$.

5.1.3.1.3 Terracotta Clay

The terracotta clay was also sourced from Western Potter Supplies, Auckland, New Zealand.

5.1.3.1.4 Subsoil

The subsoil was sourced from a residential building site in south east Auckland. The site was excavated to an approximate depth of 1 metre to accommodate the foundation. 1Kg of subsoil was removed from 1 metre below the ground surface. The soil had a mixture of clay, silica sand, organic material and water.

5.1.3.1.4 Scoria

The scoria was purchased from Winstone quarry at Three Kings, Auckland and was considered typical of a local soil matrix.

5.1.3.1.5 Limestone

The limestone is also typical white limestone decorative material supplied as (nominal) 20 mm chips. It obtained from Central Landscape & Garden Supplies 55 Springs Road, East Tamaki. It was chosen as being representative of common rocks found throughout the world.

5.1.3.1.6 Greywacke

The greywacke sandstone was a material known as "gap 7" used for roading and decorative purposes. These were obtained from Central Landscape & Garden Supplies 55 Springs Road, East Tamaki. It was chosen as being representative of common rocks found throughout the world.

5.3.1.2 Reagents

Acetone (ASCC 100%) and hexane (SIGMA 99%) were used as the extraction solvent. Octadecane was used as an internal standard and 20% phosphoric acid was used to accelerate the extraction process.

5.3.1.3 Pollutant Analogues

Naphthalene (BDH-Laboratories), 1-chloronaphthalene (ACROS Organics) and diesel from a local petrol station.

5.1.4 Methodology

5.1.4.1 Reagent Preparation

To make the extraction solvent, 500ml of hexane and acetone were poured in a 1L jar with a sealed rubber cap to prevent evaporation. 200mg of octadecane was added to the solvent mix as an internal standard.

5.1.4.2 Sample Preparation

50g of a soil sample was placed into the grinding jar. 0.25g of naphthalene/chloronaphthalene/diesel was put in a 50ml beaker and 5ml of hexane was poured. The naphthalene was stirred using a glass rod to dissolve it to the hexane. The dissolved naphthalene/hexane mix was then poured

evenly onto the soil sample within the grinding jar to make a final naphthalene concentration of 5000ppm. The grinding jar was placed in a fume hood to allow the hexane to evaporate. This was done to insure that the naphthalene was evenly spread (homogenised) around the soil sample; in order to mimic real life contamination.

When the hexane has evaporated the sample was ready to be milled.

5.1.4.3 Milling

All of the milling was done in the Retsch PM100 mill at 500rpm for all the experiments except for the moisture trial which was milled at 350rpm. The reduced milling speeds were employed in order to look for intermediates.

Twenty 20mm grinding bowls were placed into the milling jar with the pre-prepared soil sample and covered with the grinding jar top, the grinding jar was then put into the mill and fastened securely. The milling cycle was divided into five intervals of 15, 30, 60, 90, and 120 minutes. At the end of every interval one gram of the soil was removed to be extracted and analysed to determine the destruction rate of the naphthalene.

5.1.4.4 Sample Extraction

The milled sample was placed into a screw-top glass test tube, 0.5ml of 20% phosphoric acid and 5ml of the extraction solvent was added. The cap was placed on the test tube and tightly sealed and was then placed into the ultrasonic bath for 20 minutes at 30°C to augment the extraction process. After 20 minutes in the ultrasonic bath, the test tube was placed on a test tube rack and left overnight to continue extracting.

5.1.4.5 Sample Analysis

1μl of the extracted sample is injected into the GCMS to determine retention times and concentrations of the target pollutants analogues, internal standard and any intermediates.

The GCMS was programmed to have an initial oven temperature of 50°C for 3 minutes and then a temperature ramp of 20°C per minute for 10 minutes. When the oven reaches 250°C it is held at the temperature for 3 minutes.

At the end of the GCMS cycle the results are tabulated and the areas under the graph of the target organic pollutant and the internal standard are recorded to calculate the pollutant concentration.

5.2 Milling of Dried Clay

The milling of dried clay utilised and followed the same equipment and methodology as described in section 5.1 except that the soil matrices used were terracotta and china clay which were dried at varying temperatures.

Six 50g samples of each clay were measured out and dried as follows:

Terracotta Clay	China Clay
Undried	Undried
100°C	100°C
200°C	200°C
400°C	400°C
600°C	600°C
800°C	800°C

Each sample was weighed and the weight recorded before and after the drying process to determine water concentration in each sample.

The samples were milled, analysed and naphthalene concentrations calculated using the same methodology as described in section 5.1.

5.3 Moisture Trials

The milling of the moisture trials utilised and followed the same equipment, materials and methodology as described in section 5.1 except that the soil matrices used were all initially dried in an oven at 100°C overnight.

Nine 50g samples of quartz were measured out and water was added incrementally to have a final water concentration of 0, 1, 2, 3, 4, 5, 10, 20, and 60%.

Three 50g samples of scoria were measured out and water was added incrementally to have a final water concentration of 0, 2 and 5%.

Four 50g samples of limestone were measured out and water was added incrementally to have a final water concentration of 0, 2, 5 and 10%.

Each of the samples was milled, analysed and naphthalene concentrations calculated using the same methodology as described in section 5.1.

5.4 Soil Microbiology

5.4.1 Materials and Equipment

5.4.1.1 Bacteria and Soil Matrix

The bacteria used for the soil microbiology experiment were *Bacillus subtilis* and *Klebsiella pneumonia.* The soil matrix used was quartz silica sand. The bacteria and quartz were milled using the Retsch PM100 mill and the temperature of the milling jar was recorded by a thermocouple.

5.4.1.2 Dilution Equipment

- 10ml glass test tubes
- Test tube racks
- Peptone water
- *Bacillus subtilis* and *Klebsiella pneumonia* cultures
- Pipettes
- Plastic petri dishes
- Agar mix
- Magnesium Sulfate

5.4.1.3 Inoculation and Sample Preparation Equipment

- Pipettes
- Autoclave
- Inoculation loop
- 0.9% saline solution
- Incubation room

5.4.2 Methodology

5.4.2.1 Bacterial Survival During Milling

The following method sequence was used:

1. Streak plating of K. pneumonia onto normal agar plates was done to isolate colonies (fig.29).

2. Streak plating of B subtilis onto agar plate enriched with 1ppm $MnSO_4$ to induce sporulation (fig.29).

3. 50g of top soil was sieved and all organic debris was removed.

4. The soil was then autoclaved at 121°C and 15psi for 20mins.

5. After sterilisation, dry the soil sample at 150°C overnight.

6. One inoculation loopful of bacteria was suspended in 1ml of 0.9% saline.

7. Quickly pour the bacteria/saline mix into the soil sample.

8. Mix in the bacteria/saline solution homogenously into the soil.

9. The soil sample was then milled at intervals of 0 (control), 15,30,60,90 and 120mins.

10. After each interval, the temperature was measured and 1g of soil was removed and placed in 9ml of peptone water.

11. Further dilute the soil/peptone water mix to 10^{-2}.

12. 0.1ml of the diluted soil/peptone water mix was removed and surface plated onto agar plates to make a final dilution of 10^{-3}.

13. Repeat for all intervals and bacteria.

14. The inoculated agar plates were incubated at 36°C for 48 hours.

15. Conduct plate counts.

5.4.2.2 Bacterial Survival in Milled Soil

The following method sequence was used:

1. Streak plating of *K. pneumonia* onto normal agar plates was done to isolate colonies (fig.5.1).

2. Streak plating of *B. subtilis* onto agar plate enriched with 1ppm $MnSO_4$ to induce sporulation (fig.5.1).

3. 50g of top soil was sieved and all organic debris was removed.

4. The soil was then autoclaved at 121°C and 15psi for 20mins.

5. After sterilisation, dry the soil sample at 150°C overnight.

6. Prepare twelve 1ml solutions of each bacteria species to a dilution factor of 10^{-2}.

7. Mill the soil at 500rpm at intervals of 0(control), 15,30,60,90 and 120min.

8. After each interval remove 2g of soil. 1g was placed into a capped test tube and place in freezer for 15min to allow cooling and the other 1g was placed in a similar capped test tube and was left at room temperature.

9. After 15min, the sample in the freezer was removed and 1ml of the diluted bacterial solution was added to the soil sample and shook vigorously.

10. Repeat for the remaining intervals and the other bacteria species.

11. The soil samples that were left for 12 hours also had 1ml of the diluted bacterial solution added to them and shook vigorously.

12. 0.1ml from each sample was removed and streak plated onto nutrient agar plates to make a final dilution of 10^{-3}.

13. All the plates were incubated at 36°C for 48 hours and then a plate count was conducted.

Figure 5.1 - K. pneumonia and B. subtilis colonies on agar plates

5.5 Soil Fertility

5.5.1 Materials and Equipment

5.5.1.1 Soil Matrix

The soil used to test for fertility was topsoil sourced from a residential garden in south east Auckland and Kiwi Potting Mix.

The Kiwi Potting Mix contained peat moss, composted bark and sand. Both soils were mixed together. Potting mix was added topsoil to give the seeds the highest chance of germination.

The same Retsch PM100 mill described in section 5.1.1.1 was used to mill the potting mix/topsoil mixture.

5.5.1.2 Seeds

The seeds used were *Brassica nigra*, colloquially known as a type of Mustard plants. They were selected due to have a fast germination period and are able to grow in different seasons.

5.5.1.3 Pots

The pots used were half litre circular PVC pots with 4 irrigation holes to allow excess water to seep out.

5.5.1.4 Seed Grid

A 5x10 grid was made in order to plant the same number of seeds in the same pattern for the sake of replication.

5.5.2 Methodology

Three soil samples were prepared. Each of the three samples contained 250g of potting mix and 250g of topsoil; both soils were thoroughly mixed together. The first sample was left unmilled to act as the control; the second sample was milled for 2 hours and the third sample was divided into two and one half was milled and other half was not. The two halves were then mixed together.

Each sample was then placed into a pot and 50 seeds were planted into each one using the 5x10 seed grid (fig. 5.2).
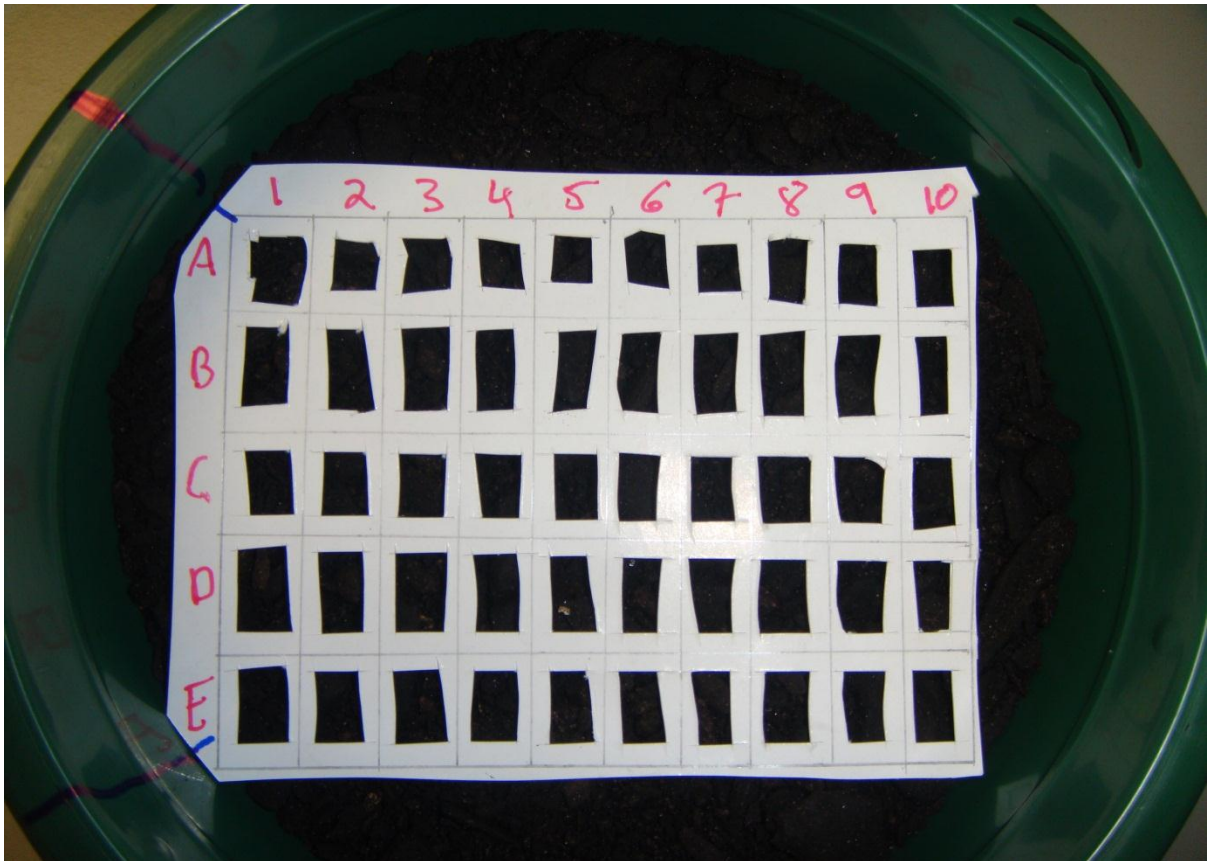
Figure 5.2 – Picture of the seed grid

The pots were placed in a sunny area and were watered twice a day with 150ml of water. A daily photographic record of the plants' growth was kept.

Chapter 6 – Results and Discussion
6.1 Contaminants Destruction in Different Soils

Naphthalene was milled in different soils in an effort to determine whether different soils had an effect on destruction efficiency. The soils used in this study were terracotta clay, china clay, greywacke, limestone, scoria, quartz and subsoil.

6.1.1 Terracotta Clay

Naphthalene Destruction in Terracotta Clay
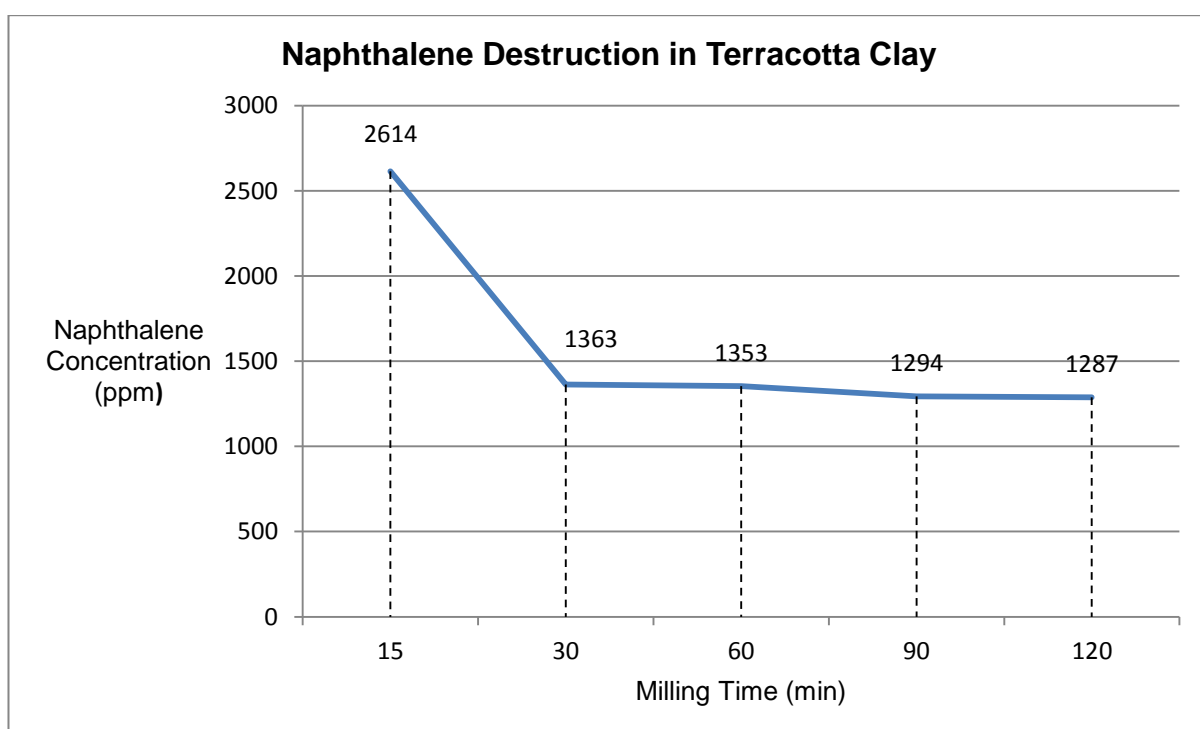
A steep decline in naphthalene destruction is observed from 0 to 30 minutes, followed by a plateau to 120 minutes. The reason for this plateau is thought to be due to the high water content of the clay.

Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	2614	48
30	1363	72
60	1353	73
90	1294	74
120	1287	74

6.1.2 China Clay

Naphthalene Destruction in China Clay
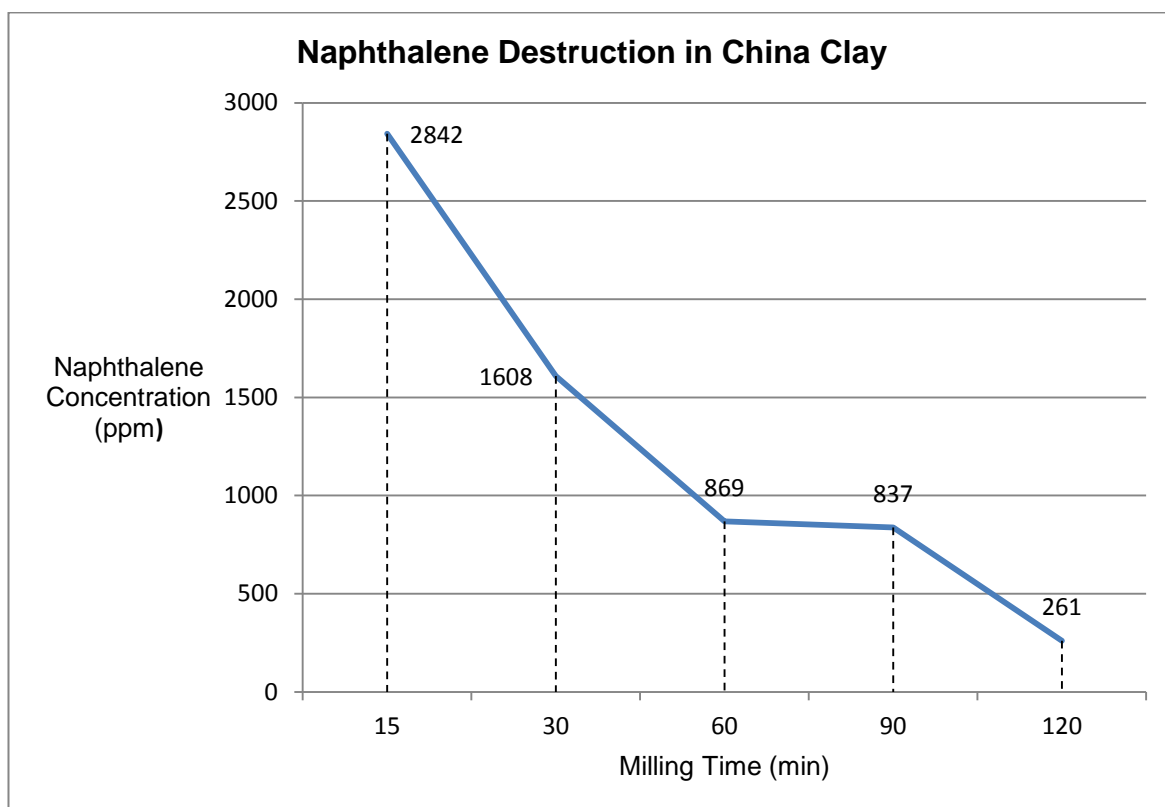
Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	2842	43
30	1608	68
60	869	83
90	837	83
120	261	95

China clay had the second strongest effect on the destruction efficiency. Destruction of naphthalene was observed throughout all milling intervals, i.e. no plateau was observed.

6.1.3 Greywacke

Naphthalene Destruction in Greywacke
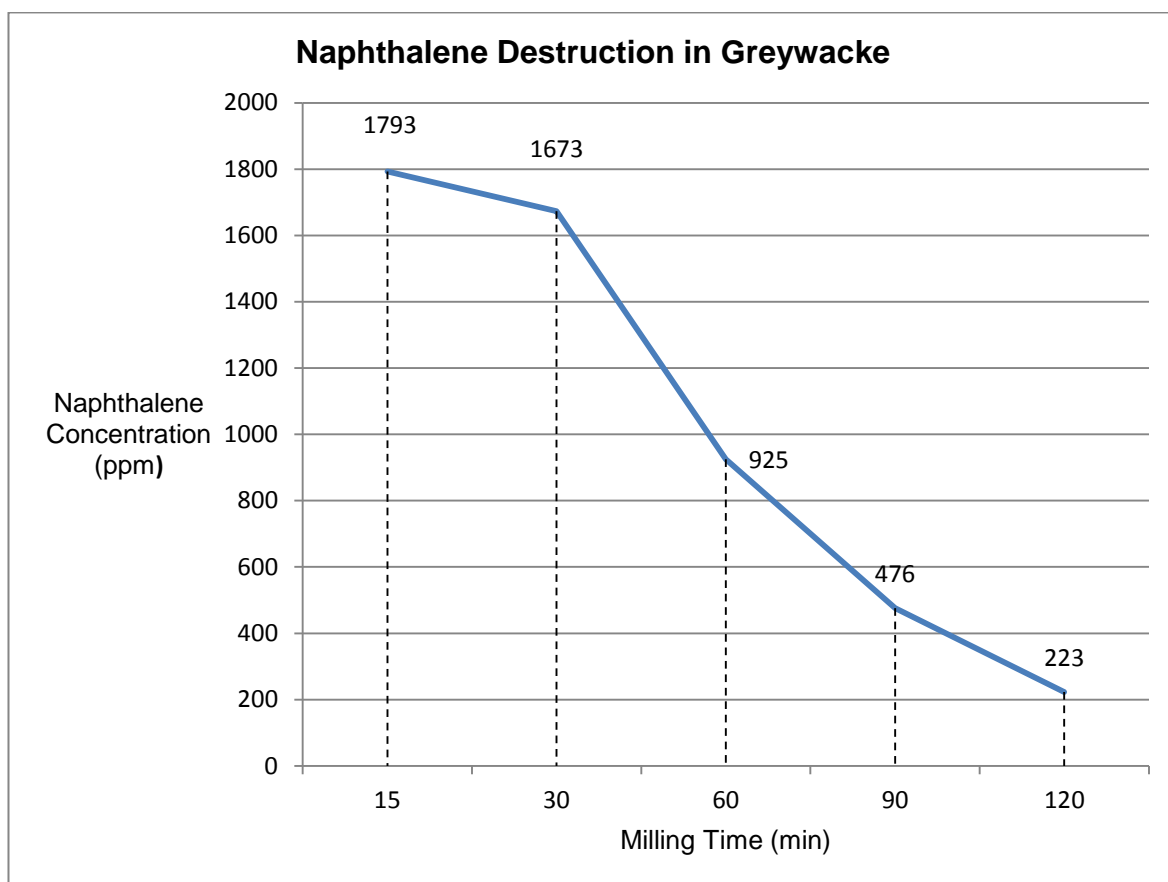
Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	1793	64
30	1673	67
60	925	82
90	476	90
120	223	96

The destruction of naphthalene in greywacke was consistent throughout the milling intervals. It performed better than both clays due to its very low water content and to its hardness.

6.1.4 Quartz

Naphthalene Destruction in Quartz
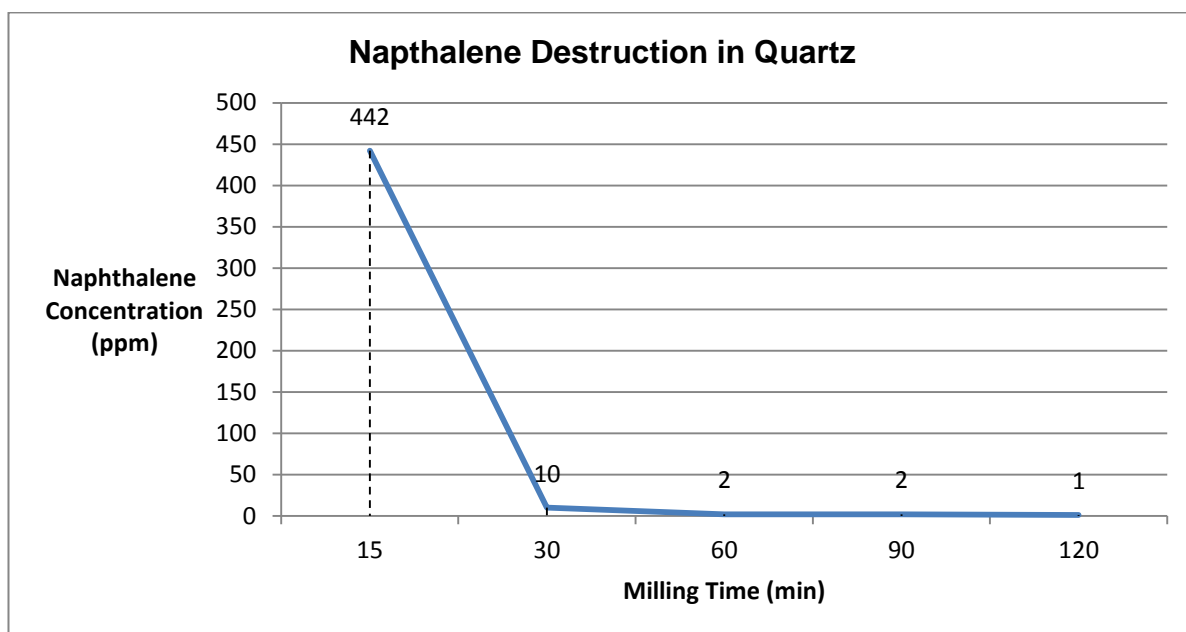
Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	442	91
30	10	99.80
60	2	99.96
90	2	99.96
120	1	99.98

When milling with quartz, the destruction rate at the end of the first milling interval (15min) was over 90%. At the second milling interval, the destruction rate of naphthalene was nearly 100%. These high destruction rates were only observed in quartz. Early conclusions can be made that contaminated sites with high percentage of quartz in their soils are good candidates for mechanochemical remediation.

6.1.5 Scoria
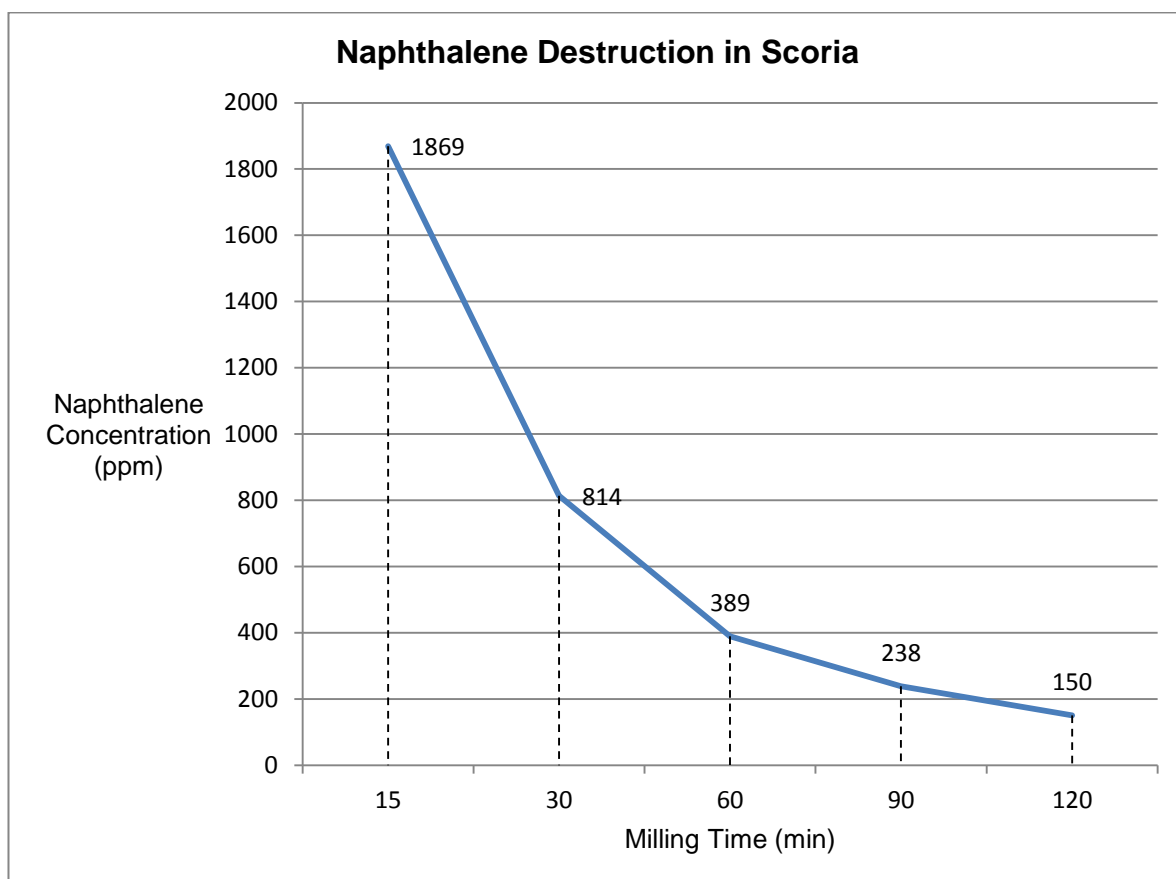
Naphthalene Destruction in Scoria

Naphthalene Concentration (ppm)

Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	1869	63
30	814	84
60	389	92
90	238	95
120	150	97

Overall, scoria was the second best performer after quartz. This is attributed to its very low water content and its hardness. By the end of the milling cycle, scoria had a 97% destruction rate of naphthalene.

6.1.6 Limestone

Naphthalene Destruction in Limestone
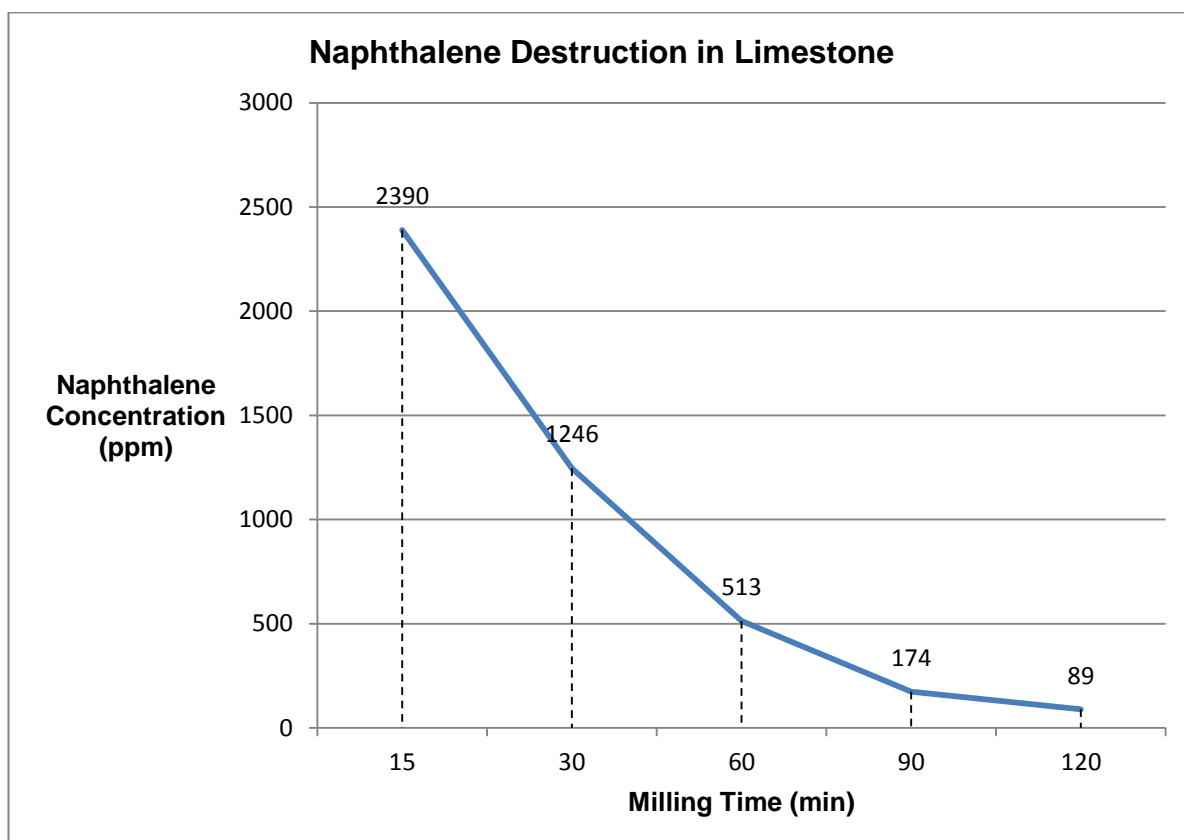
Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	2390	52
30	1326	73
60	513	90
90	174	97
120	89	98

Limestone is a sedimentary rock composed largely of calcite and aragonite which are different crystal forms of calcium carbonate. It was efficient in terms of naphthalene destruction. It also had consistent destruction rate overtime with no plateau reached.

6.1.7 Sub Soil – Stored at Room Temperature
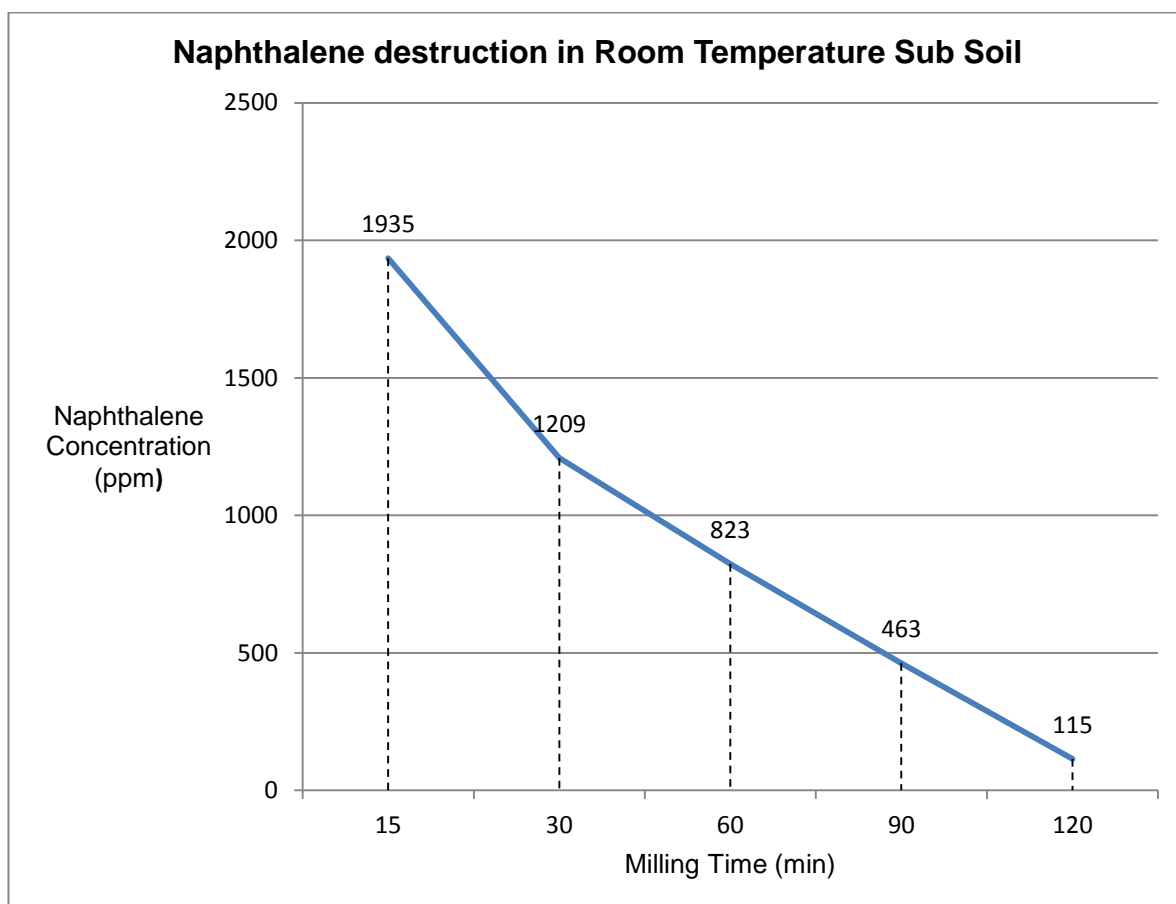
Naphthalene destruction in Room Temperature Sub Soil

Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	1935	61
30	1209	76
60	823	84
90	463	91
120	115	98

The subsoil demonstrated a consistent naphthalene destruction rate, but is not as efficient as quartz, scoria or even limestone. The high water content is thought to have decreased the destruction rate.

6.1.8 Sub Soil – Dried at 700°C

Naphthalene Destruction in Sub Soil Dried at 700°C

Naphthalene Concentration (ppm) vs Miling Time (min)
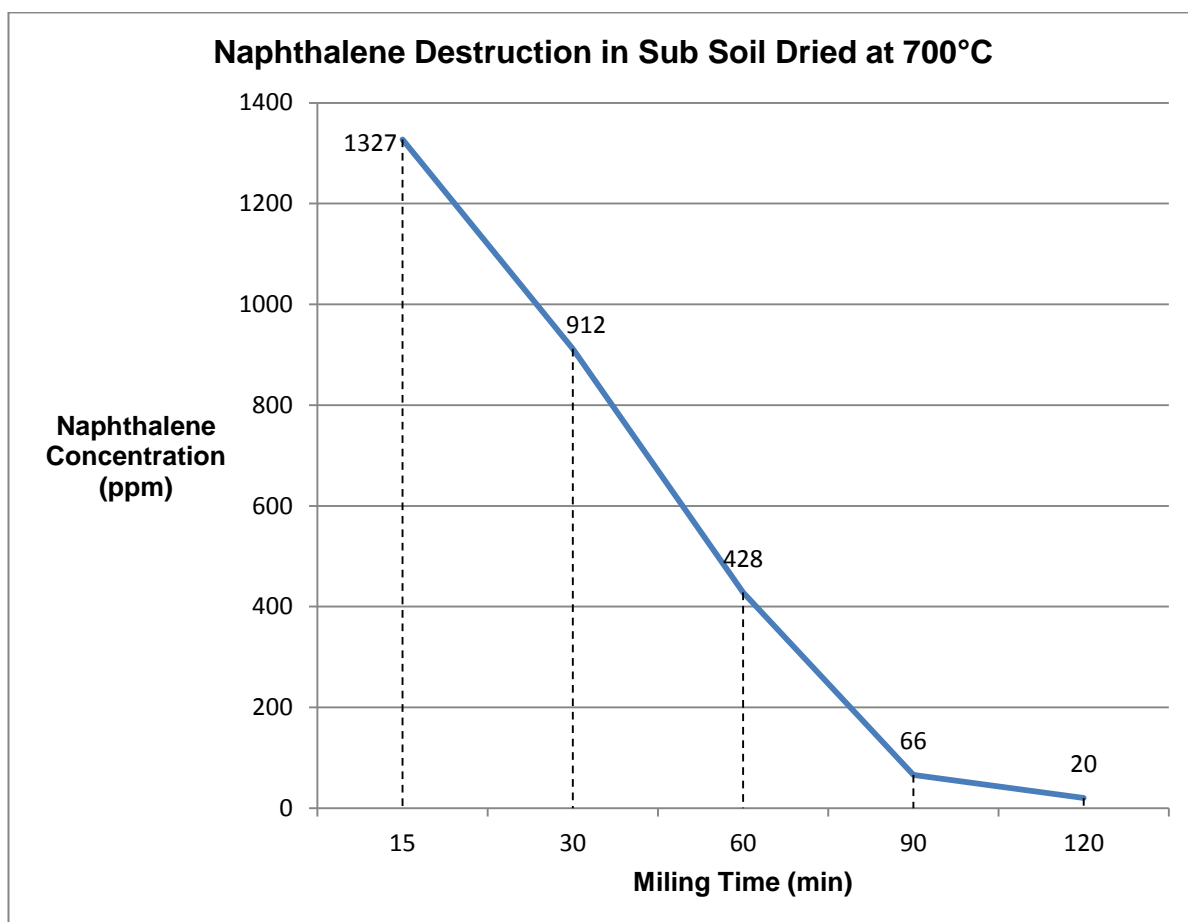
- 1327
- 912
- 428
- 66
- 20

Milling Interval (min)	Naphthalene Conc. (ppm)	Destruction Rate (%)
0	5000	0
15	1327	73
30	1317	74
60	428	91
90	66	98
120	20	99

Subsoil was dried at 700°C to remove all the free and bounded water in the clay. The destruction rate was much higher over all the milling intervals compared to the room temperature subsoil.

6.1.9 Discussion

Naphthalene Abundance in Different Soils

Naphthalene Destruction rates in Different Soils
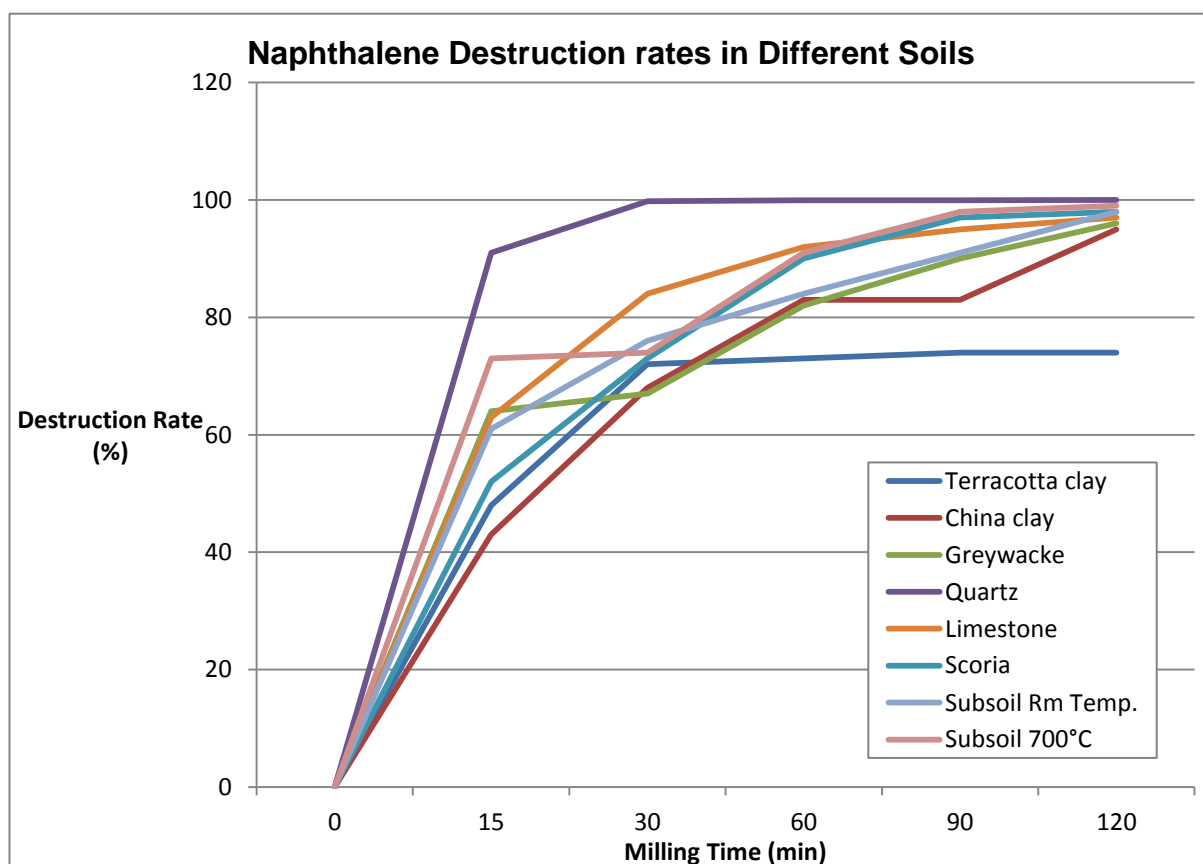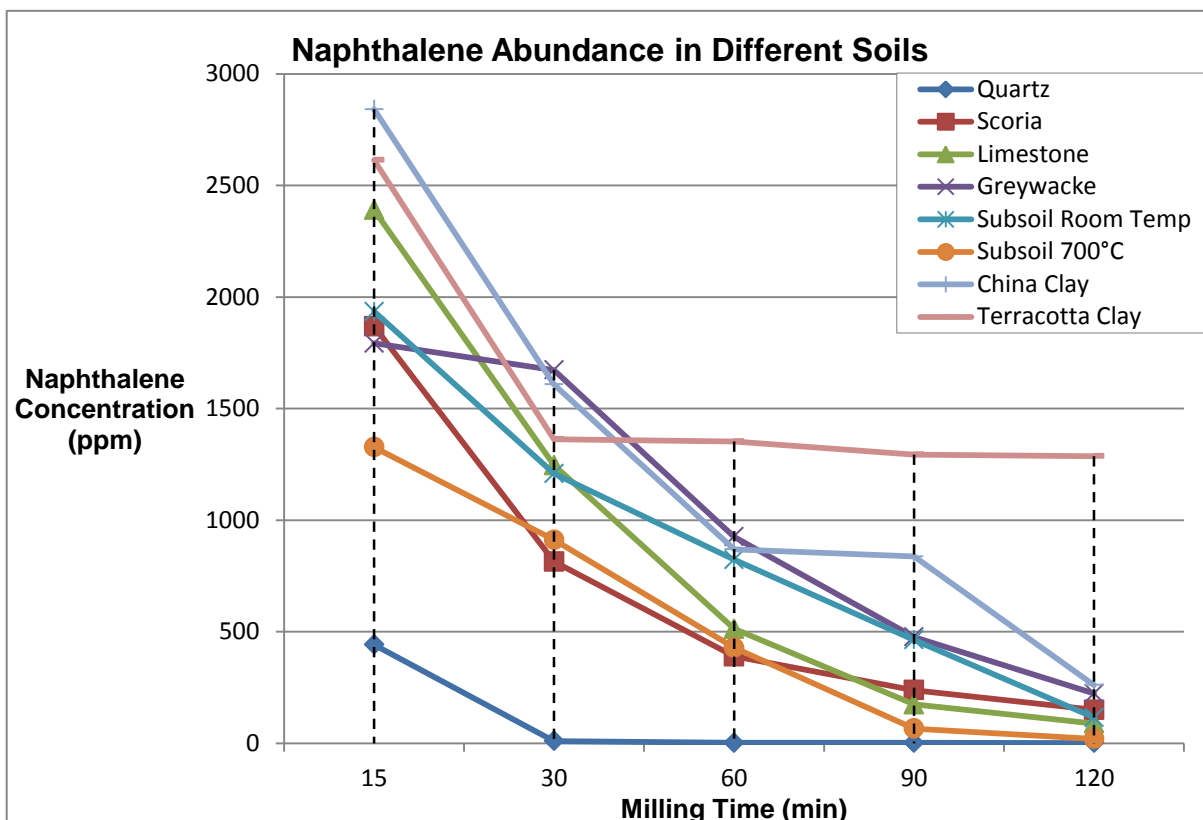
In the naphthalene abundance graph, there are three distinct trends. The most efficient soil is quartz, it yielded the highest destruction rate throughout all milling intervals and only tiny amounts of naphthalene remained after 30 minutes of milling. The second trend is made up of scoria, limestone, greywacke, china clay and both sub soils. These soils all exhibited inversely proportional destructions rates of similar magnitudes after the 30 minute interval. By 120 minutes all the soils yielded similar destruction rates; a variation between 20ppm and 261ppm. The third trend consists of the terracotta clay. After an initial decline in naphthalene concentration during the first milling interval, the concentration then plateaued. This was due to the internal temperature of the grinding jar during milling. The temperature reaches the boiling point of water at the 30 minute interval and all the free water in the clay is evaporated. This loss of free water increased the destruction rate to a certain extent, but the remaining bound water hinders the destruction rate and kept the naphthalene concentration nearly constant.

The naphthalene destruction rate graph shows the destruction rates in terms of how much naphthalene remained from time zero to each milling interval. It mirrors the naphthalene abundance graphs; terracotta clay destruction rates plateau between the 72% and 74% range (in milling intervals 30, 60, 90 and 120 minutes) which translates to the abundance range between 1363ppm to 1287ppm range. Another plateau is also depicted, but due to opposite reasons; quartz destruction rates plateau between the 99.8% and 99.98% range (in milling intervals 30, 60, 90 and 120 minutes) which translates to the abundance range between 10ppm to 1ppm from a total concentration of 5000ppm at time 0.

6.2 Clay Drying Experiment

From section 5.1, it is evident that clays do not perform very well in terms of destruction efficiency. This experiment was designed to determine whether water content is the main reason for this phenomenon. Sample of Terracotta and China clay were dried at varying temperatures and milled with naphthalene at intervals of 15, 30, 60, 90 and 120 minutes to test hypothesis.

6.2.1 China Clay

Six 50g samples China clay was dried at 100, 200, 400, 600, 800°C and one was kept at room temperature (as received) to serve as a control. To each sample 5000ppm of naphthalene was added and was milled.

6.2.1.1 Control

6.2.1.2 Died at 100°C
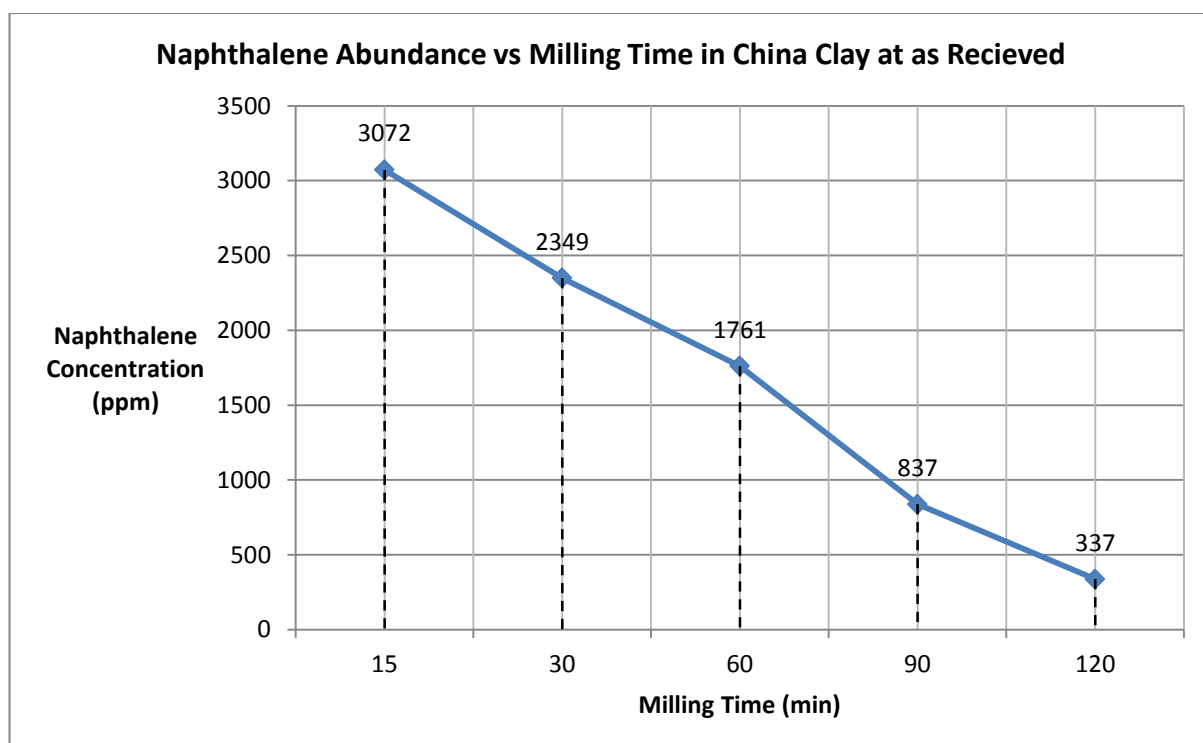
Naphthalene Abundance vs Milling Time in China Clay Dried at 100°C

6.2.1.3 Dried at 200°C
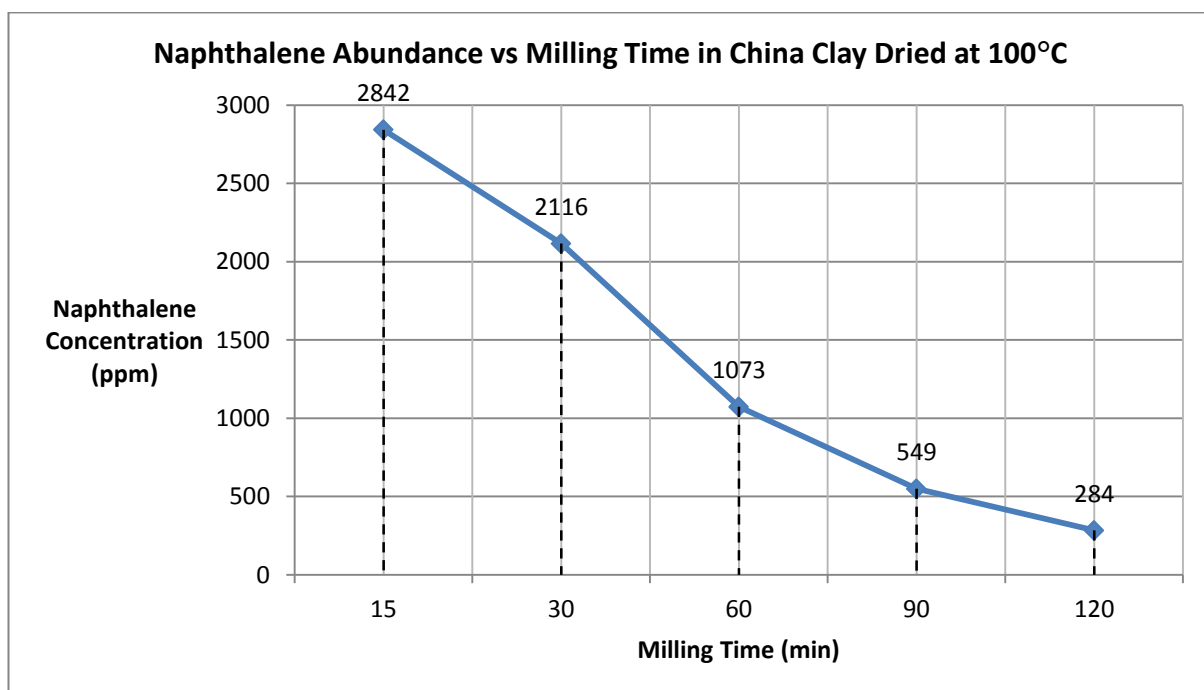
Naphthalene Abundance vs Milling Time in China Clay Dried at 200°C

6.2.1.4 Dried at 400°C

Naphthalene Abundance vs Milling Time in China Clay Dried at 400°C

Naphthalene Concentration (ppm)

- 2566
- 1836
- 785
- 279
- 31

Milling Time (min): 15, 30, 60, 90, 120

6.2.1.5 Dried at 600°C

Naphthalene Abundance vs Milling Time in China Clay Dried at 600°C

Naphthalene Concentration (ppm)

- 2215
- 1608
- 767
- 51
- 20

Milling Time (min): 15, 30, 60, 90, 120

6.2.1.6 Dried at 800°C
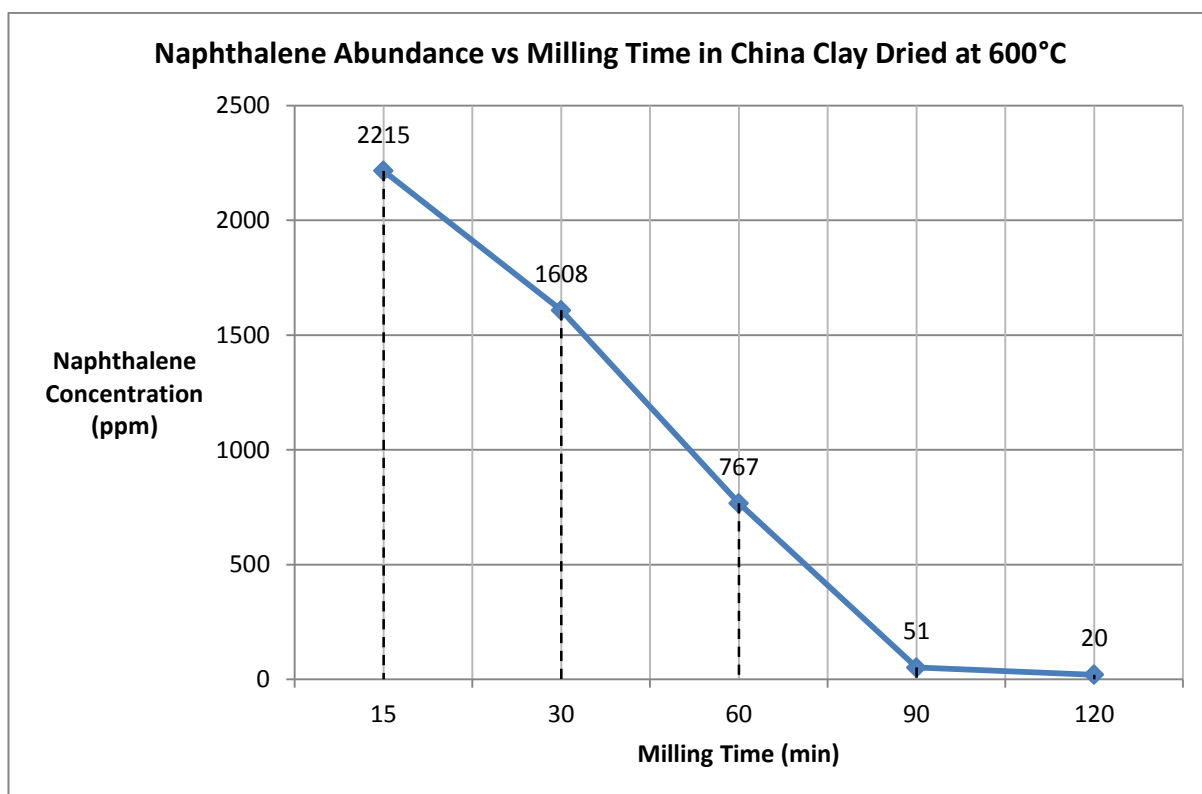
Naphthalene Abundance vs Milling Time in China Clay Dried at 800°C

6.2.1.7 Discussion

Milling Interval (min)	Room Temp Naphthalene Conc. (ppm)	Room Temp Destruction Rate (%)
0	5000	0
15	3072	39
30	2349	53
60	1761	65
90	837	83
120	337	93

Milling Interval (min)	Dried at 100C Naphthalene Conc. (ppm)	Dried at 100C Destruction Rate (%)
0	5000	0
15	2842	43
30	2116	58
60	1073	79
90	549	89
120	284	94

Milling Interval (min)	Dried at 200C Naphthalene Conc. (ppm)	Dried at 200C Destruction Rate (%)
0	5000	0
15	2776	45
30	2106	58
60	869	83
90	546	89
120	261	95

Milling Interval (min)	Dried at 400C Naphthalene Conc. (ppm)	Dried at 400C Destruction Rate (%)
0	5000	0
15	2566	49
30	1836	63
60	785	84
90	279	94
120	31	99

Milling Interval (min)	Dried at 600C Naphthalene Conc. (ppm)	Dried at 600C Destruction Rate (%)
0	5000	0
15	2215	56
30	1608	68
60	767	85
90	51	99
120	20	99

Milling Interval (min)	Dried at 800C Naphthalene Conc. (ppm)	Dried at 800C Destruction Rate (%)
0	5000	0
15	1951	61
30	1522	70
60	430	91
90	37	99
120	4	100

Naphthalene Abundance vs Milling Time in China Clay Dried at Varying Temperatures
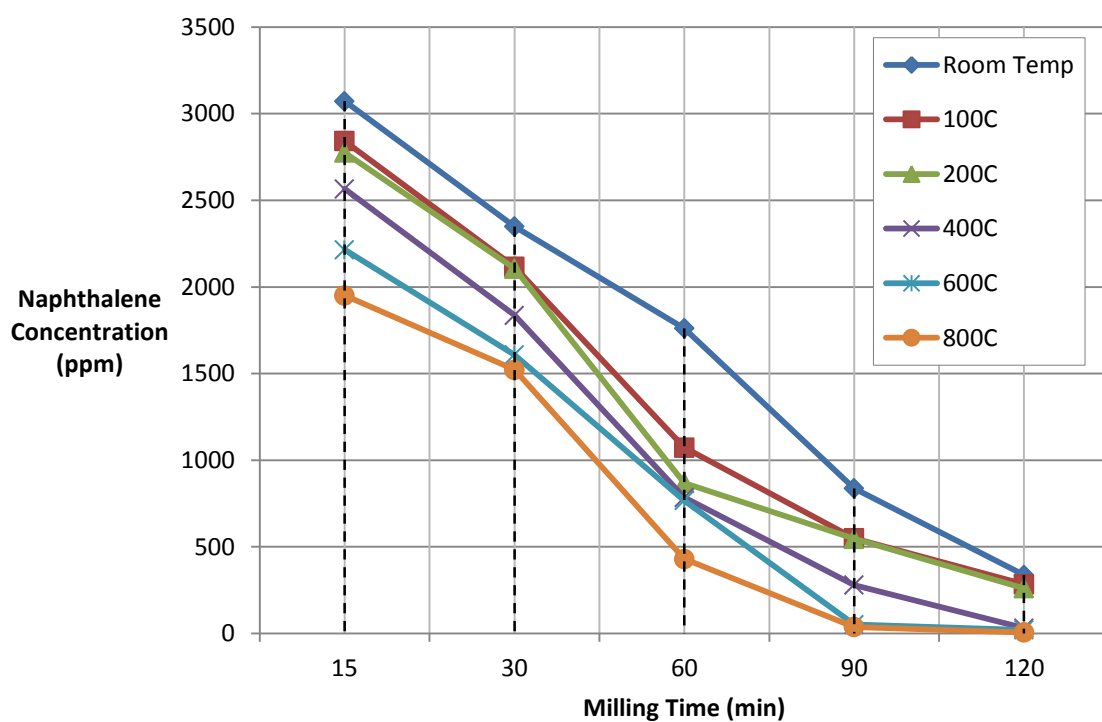
Destruction Rates versus Drying Temperatures
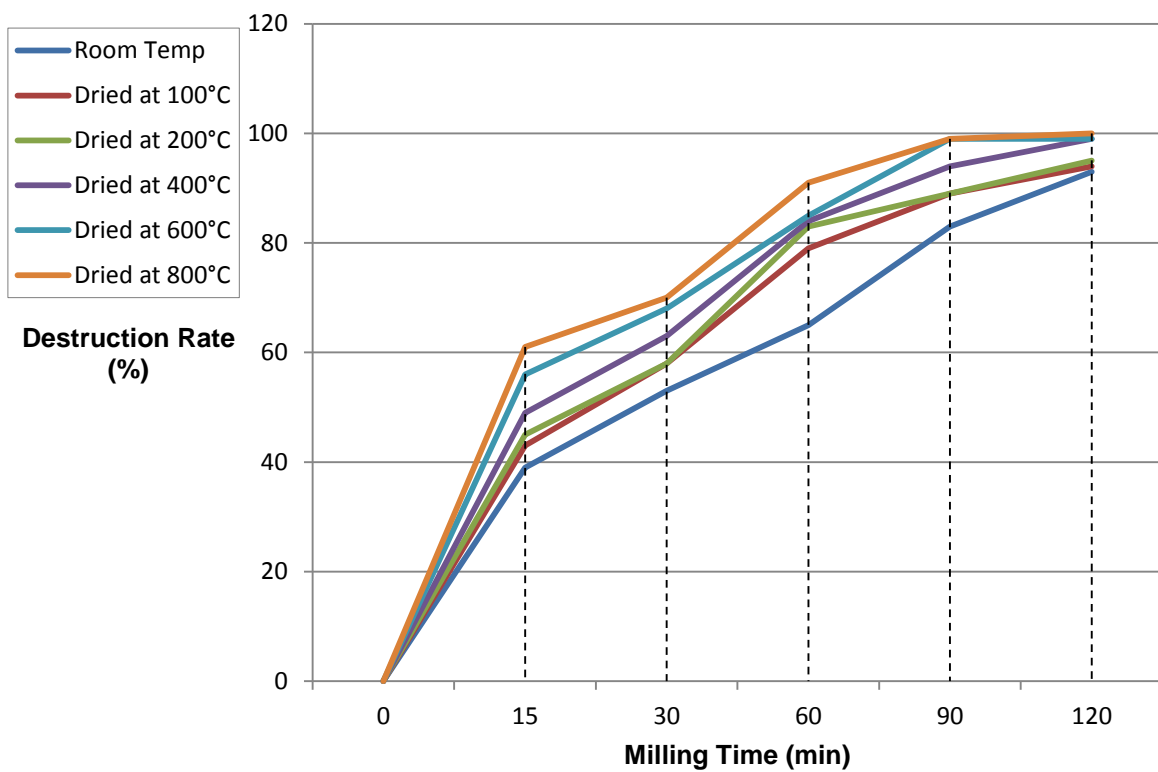
All the data follows the same trend of gradual destruction over time. There is also an overall trend of increased destruction with the increase of drying temperature. China clay does not have as much water as terracotta clay and clay found in soil, therefore the drying effect did not greatly increase the destruction rate of naphthalene.

Furthermore China clay has extremely low organic and other materials that would hinder the destruction rates. Therefore, there was no marked increase in naphthalene destruction at temperatures of 600 and 800°C; at these temperatures any organic matter would be completely degraded.

6.2.2 Terracotta Clay

Six 50g samples Terracotta clay was dried at 100, 200, 400, 600, 800°C and one was kept at room temperature to serve as a control. To each sample 5000ppm of naphthalene was added and was milled.
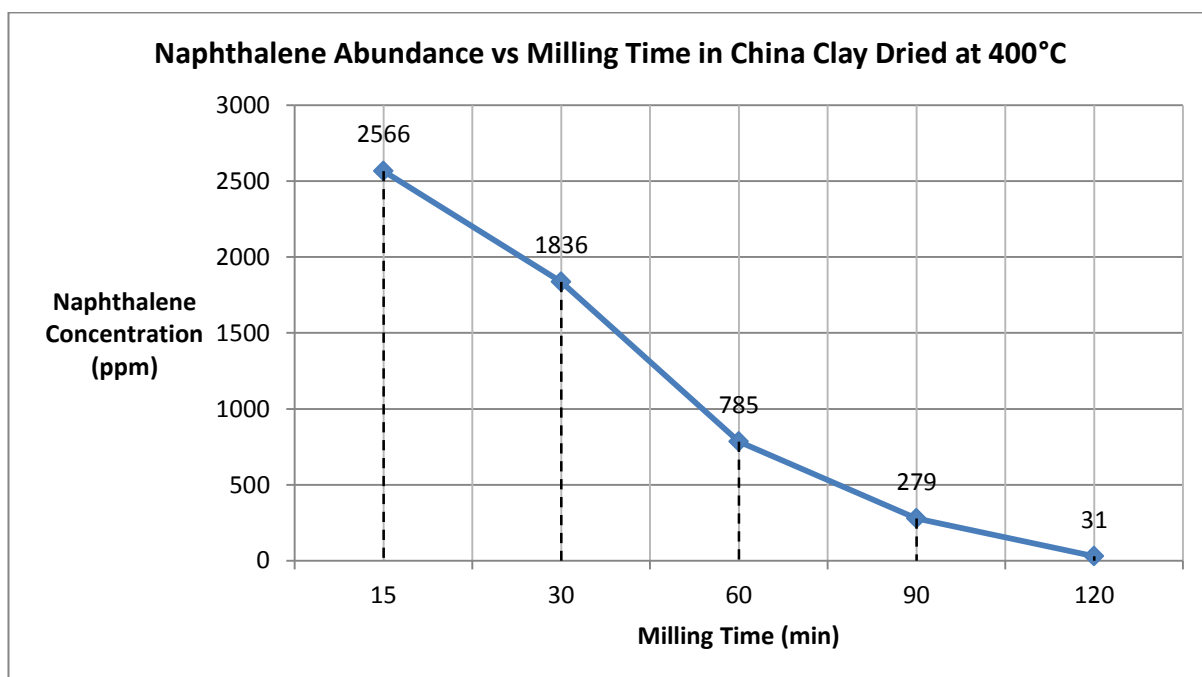
6.2.2.1 Room Temperature

Naphthalene Abundance vs Milling Time in Terracota Clay at Room Temperature

6.2.2.2 Dried at 100°C
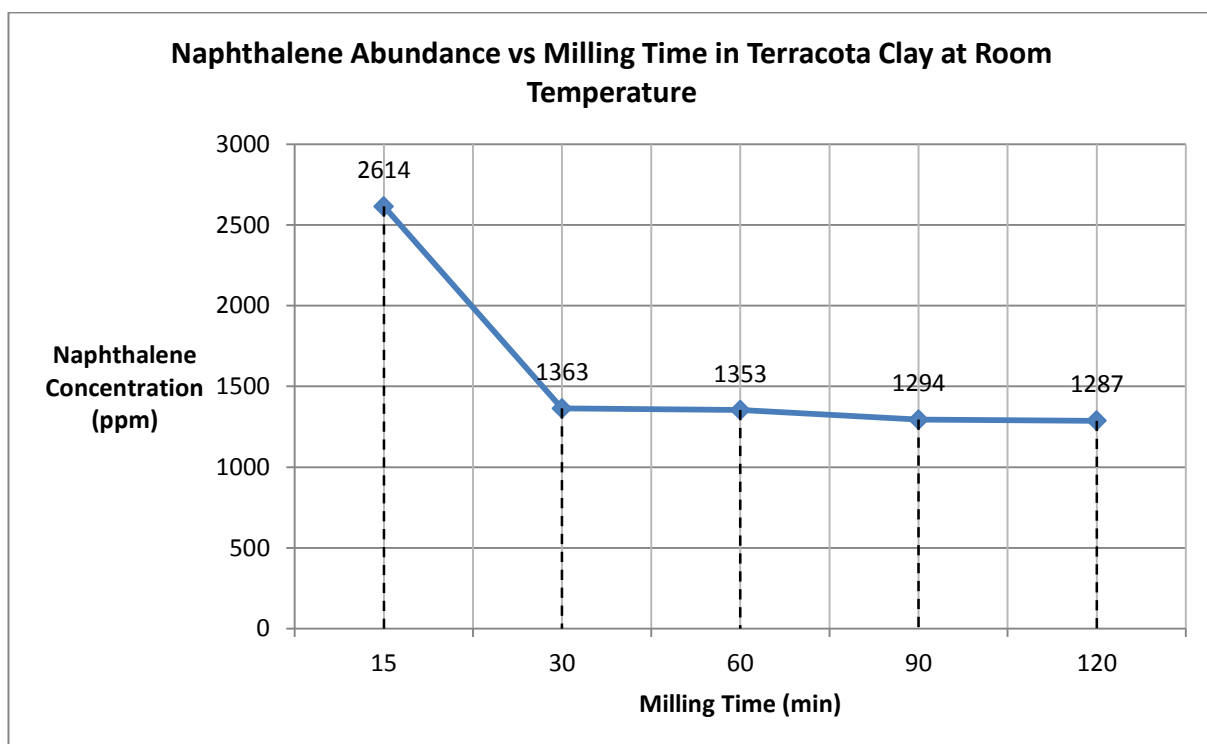
Naphthalene Abundance vs Milling Time in Terracota Clay Dried at 100C

6.2.2.3 Dried at 200°C

Naphthalene Abundance vs Milling Time in Terracota Clay Dried at 200C

Naphthalen Concentration (ppm)

- 2251
- 1742
- 952
- 627
- 282

Milling Time (min): 15, 30, 60, 90, 120

6.2.2.4 Dried at 400°C

Naphthalene Abundance vs Milling Time in Terracota Clay Dried at 400C

Naphthalene Concentration (ppm)

- 2509
- 2075
- 868
- 381
- 132

Milling Time (min): 15, 30, 60, 90, 120

6.2.2.5 Dried at 600°C
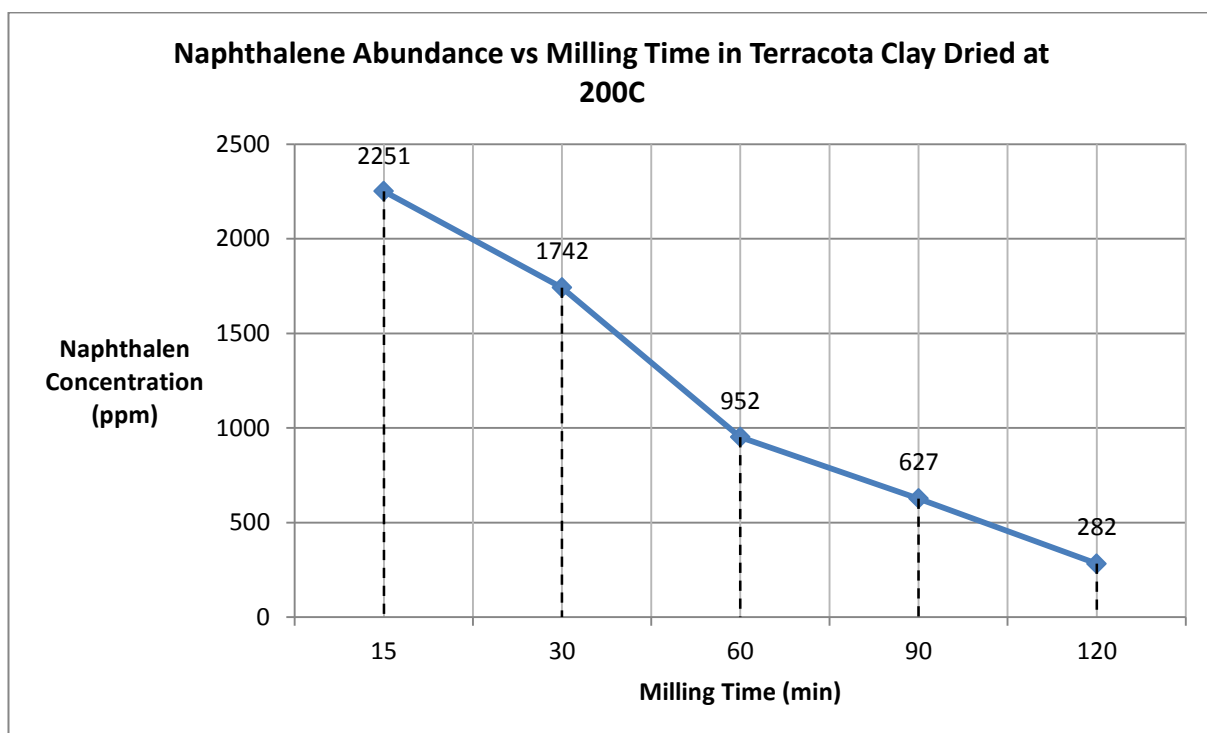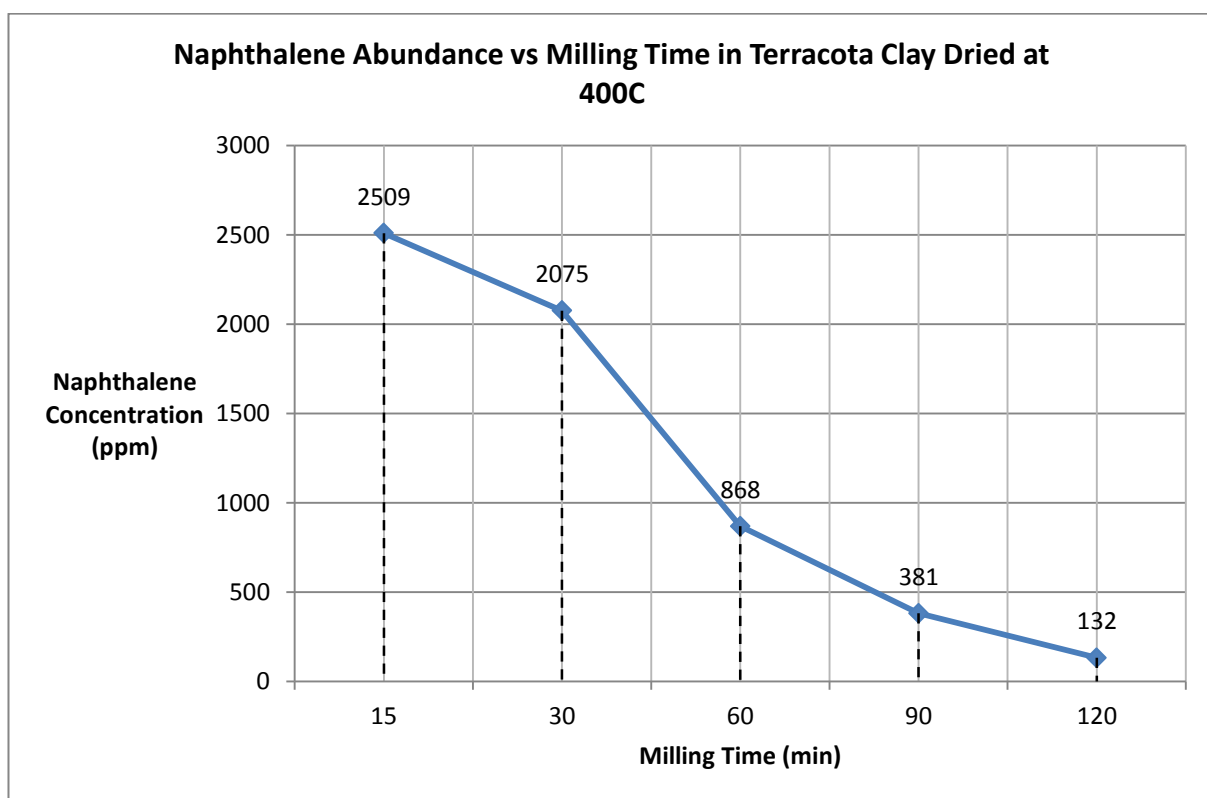
Naphthalene Abundance vs Milling Time in Terracota Clay Dried at 600C

6.2.2.6 Dried at 800°C
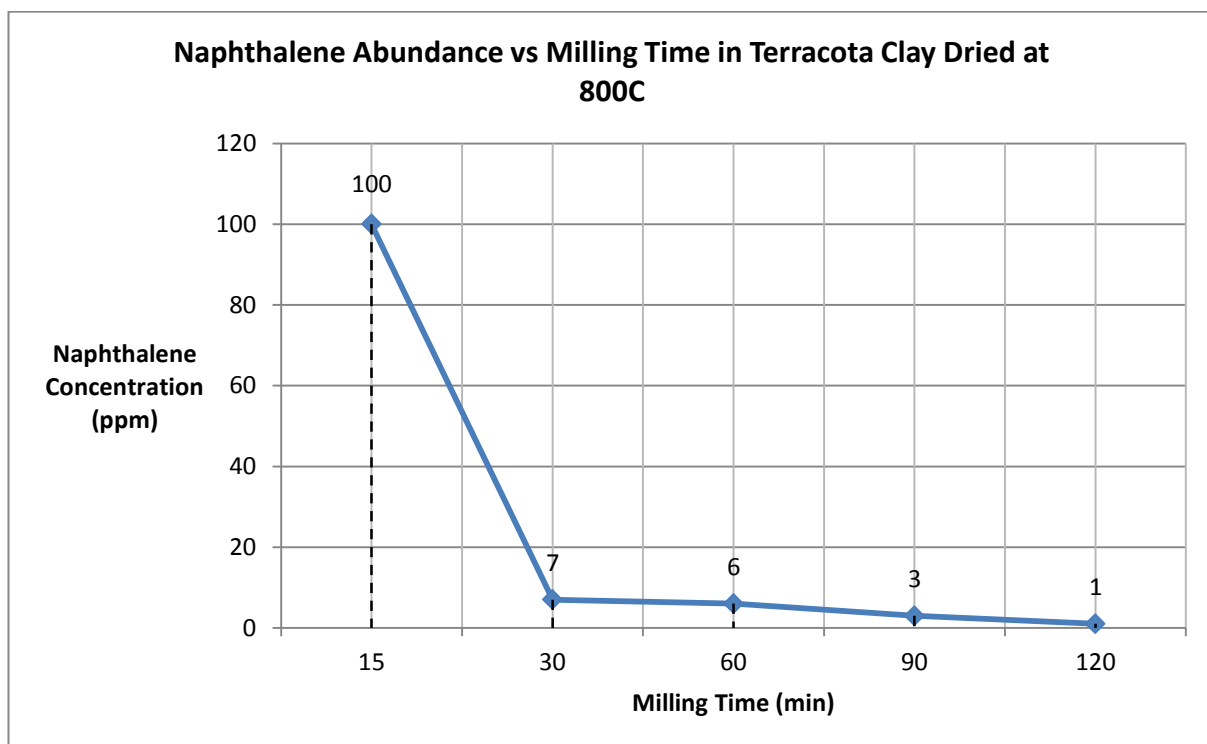
Naphthalene Abundance vs Milling Time in Terracota Clay Dried at 800C

6.2.2.7 Discussion

Milling Interval (min)	Room Temp Naphthalene Conc. (ppm)	Room Temp Destruction Rate (%)
0	5000	0
15	2614	48
30	1363	73
60	1353	73
90	1294	74
120	1287	74
Milling Interval (min)	Dried at 100C Naphthalene Conc. (ppm)	Dried at 100C Destruction Rate (%)
0	5000	0
15	2288	54
30	2096	58
60	1149	77
90	441	91
120	29	99
Milling Interval (min)	Dried at 200C Naphthalene Conc. (ppm)	Dried at 200C Destruction Rate (%)
0	5000	0
15	2251	55
30	1742	65
60	952	81
90	627	87
120	282	94
Milling Interval (min)	Dried at 400C Naphthalene Conc. (ppm)	Dried at 400C Destruction Rate (%)
0	5000	0
15	2509	50
30	2075	59
60	868	83
90	381	92
120	132	97
Milling Interval (min)	Dried at 600C Naphthalene Conc. (ppm)	Dried at 600C Destruction Rate (%)
0	5000	0
15	176	96
30	55	99
60	5	100
90	4	100
120	4	100
Milling Interval (min)	Dried at 800C Naphthalene Conc. (ppm)	Dried at 800C Destruction Rate (%)
0	5000	0
15	100	98
30	7	100
60	6	100
90	3	100
120	1	100

Naphthalene Abundance vs Milling Time in Terracota Clay
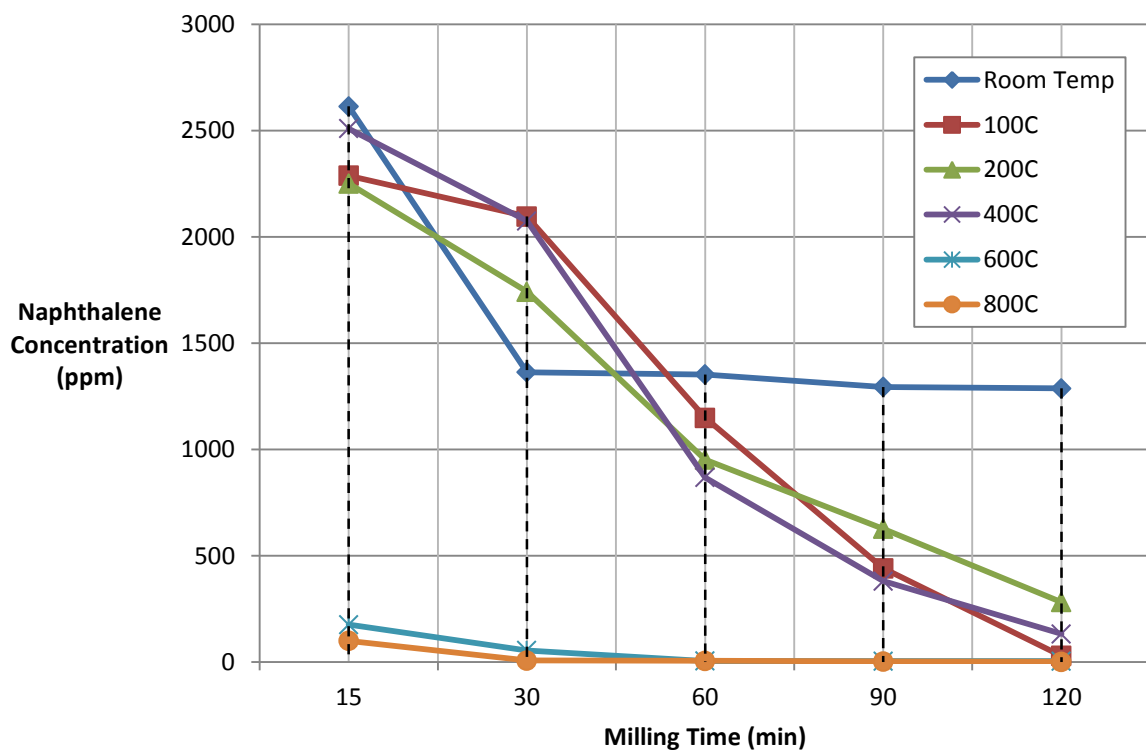
Destruction Rate of Naphthalene in Terracotta Clay Dried at Different Temperatures
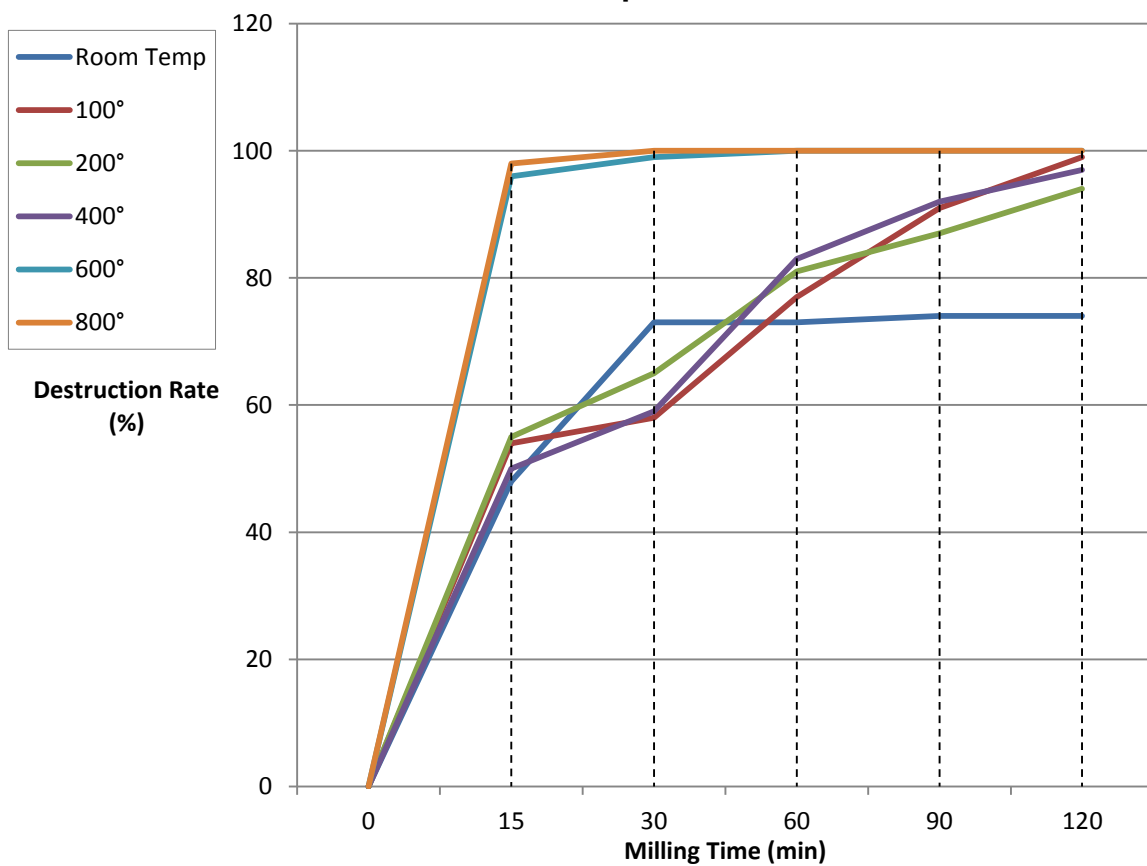
Once again, like in section 5.1, there is an emergence of three over all trends. The first trend consists of the samples dried at 600°C and 800°. They exhibit very rapid destruction that is attributed to the complete removal of free water and bonded water in the clay. Clay can be characterised as being a molecule of alumina and two molecules of silica bonded with two molecules of water.

This bonded water requires much more energy to remove (much higher than atmospheric water's boiling point of 100°C). The bonded water remains after all the atmospheric water is gone. At 100°C, the clay still contains some 14% of chemically bonded water by weight. Drying between 600°C and 800°C will remove the bonded water and will also burn off any carbon, organic materials, and sulfur.

The second trend consists of the clays dried at 100°C, 200°C and 400°C. This group depicts similar over all destruction trends throughout all the milling intervals. Even all the free water within the clay has been dried, the bonded water still remains. This is mirrored by the decreased destruction rates of these clays when compared to the two clays dried at higher temperatures. Bonded water molecules are only removed at these high temperatures.

The third trend consists of the control sample which was not dried and milled at room temperature. The clay was very wet and the destruction efficiency was poor. There was an initial decrease in naphthalene concentration from intervals 15 to 30 minutes, but after that the destruction efficiency plateaued.

6.3 Moisture Trials

From section 5.2, it is clear that the reason why clay exhibits very poor destruction efficiency or organic molecules is due to the water. However, it is not known whether the poor destruction rates are purely due to the water's interaction with the generated active species or whether clay's make up of aluminium silicates of varying amounts of iron, magnesium, alkali metals, alkaline earths and other cations has something to do with it. To test for this, different soils were moistened with varying concentrations of water and milled to measure the destruction efficiency.

6.3.1 Quartz Moisture Trial

Four 50g samples of quartz were dried at 100°C overnight to remove all free water. Then three of the samples were moistened with water at concentrations of 1%, 2%, 3%, 4%, 5%, 10%, 20%, 40% and 60% by weight and one was left dry to serve as the control.

6.3.1.1 Quartz Dried at 100°C With No Added Water

Naphthalene Destruction in Quartz with 0% water content

6.3.1.2 Quartz 1% Water

Naphthalene destruction in Quartz with 1% Water Content

Naphthalene Concentration (ppm) vs Milling Time (min)

Data points:
- 15 min: 1399
- 30 min: 1440
- 60 min: 1243
- 90 min: 803
- 120 min: 197

6.3.1.3 Quartz 2% Water

Naphthalene Destruction in Quartz with 2% Water Content

Naphthalene Concentration (ppm) vs Milling Time (min)

Data points:
- 15 min: 1791
- 30 min: 1355
- 60 min: 1297
- 90 min: 717
- 120 min: 230

6.3.1.4 Quartz 3% Water

Naphthalene Destruction in Quartz with 3% Water Content

Naphthalene Concentration (ppm)

1765
1078
980
644
228

Milling Time (min): 15, 30, 60, 90, 120

6.3.1.5 Quartz 4% Water

Naphthalene Destruction in Quartz with 4% Water Content

Naphthalene Concentration (ppm)

2152
2022
1872
876
228

Milling Time (min): 15, 30, 60, 90, 120

6.3.1.6 Quartz 5% Water

Naphthalene Destruction in Quartz with 5% Water Content

6.3.1.7 Quartz 10% Water

Naphthalene Destruction in Quartz with 10% Water Content

6.3.1.8 Quartz 20% Water

Naphthalene Destruction in Quartz with 20% water Content

6.3.1.9 Quartz 40% Water

Naphthalene Destruction in Quartz with 40% Water Content

6.3.1.10 Quartz 60% Water

Naphthalene Destruction in Quartz with 60% Water Content

6.3.1.11 Discussion

Milling Interval (min)	No Added Water Naphthalene Conc. (ppm)	No Added Water Destruction Rate (%)
0	5000	0
15	837	83
30	720	86
60	107	98
90	47	99
120	28	99

Milling Interval (min)	1% Water Naphthalene Conc. (ppm)	1% Water Destruction Rate (%)
0	5000	0
15	1399	72
30	1440	71
60	1243	75
90	803	84
120	197	96

Milling Interval (min)	2% Water Naphthalene Conc. (ppm)	2% Water Destruction Rate (%)
0	5000	0
15	1791	64
30	1355	73
60	1297	74
90	717	86
120	230	95

Milling Interval (min)	3% Water Naphthalene Conc. (ppm)	3% Water Destruction Rate (%)
0	5000	0
15	1765	65
30	1078	78
60	980	80
90	644	87
120	228	95

Milling Interval (min)	4% Water Naphthalene Conc. (ppm)	4% Water Destruction Rate (%)
0	5000	0
15	2152	57
30	2022	60
60	1872	63
90	876	82
120	228	95

Milling Interval (min)	5% Water Naphthalene Conc. (ppm)	5% Water Destruction Rate (%)
0	5000	0
15	2347	53
30	944	81
60	909	82
90	681	86
120	340	93

Milling Interval (min)	10% Water Naphthalene Conc. (ppm)	10% Water Destruction Rate (%)
0	5000	0
15	1824	64
30	1404	72
60	488	90
90	389	92
120	132	97

Milling Interval (min)	20% Water Naphthalene Conc. (ppm)	20% Water Destruction Rate (%)
0	5000	0
15	2205	56
30	2096	58
60	1662	67
90	870	83
120	244	95

Milling Interval (min)	40% Water Naphthalene Conc. (ppm)	40% Water Destruction Rate (%)
0	5000	0
15	1688	66
30	1609	68
60	1298	74
90	1127	77
120	793	84

Milling Interval (min)	60% Water Naphthalene Conc. (ppm)	60% Water Destruction Rate (%)
0	5000	0
15	2278	54
30	1680	66
60	1566	67
90	1521	70
120	1462	71

Naphthalene Destruction vs Milling Time at Different Water Content at 350rpm
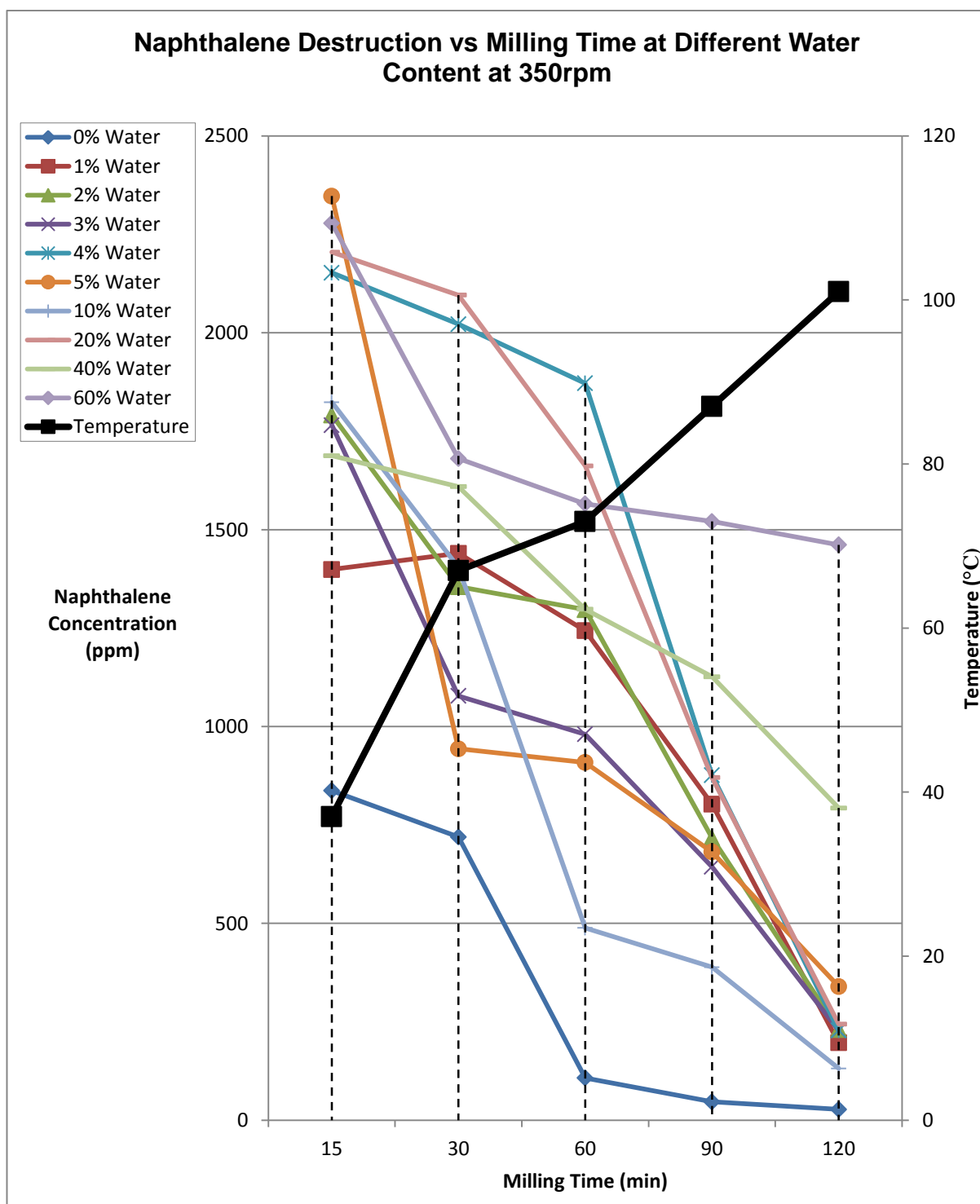
Naphthalene Destruction Rate in Quartz at Different Water Concentrations

Mill Interval Destruction Rates vs Water concentration in Quartz
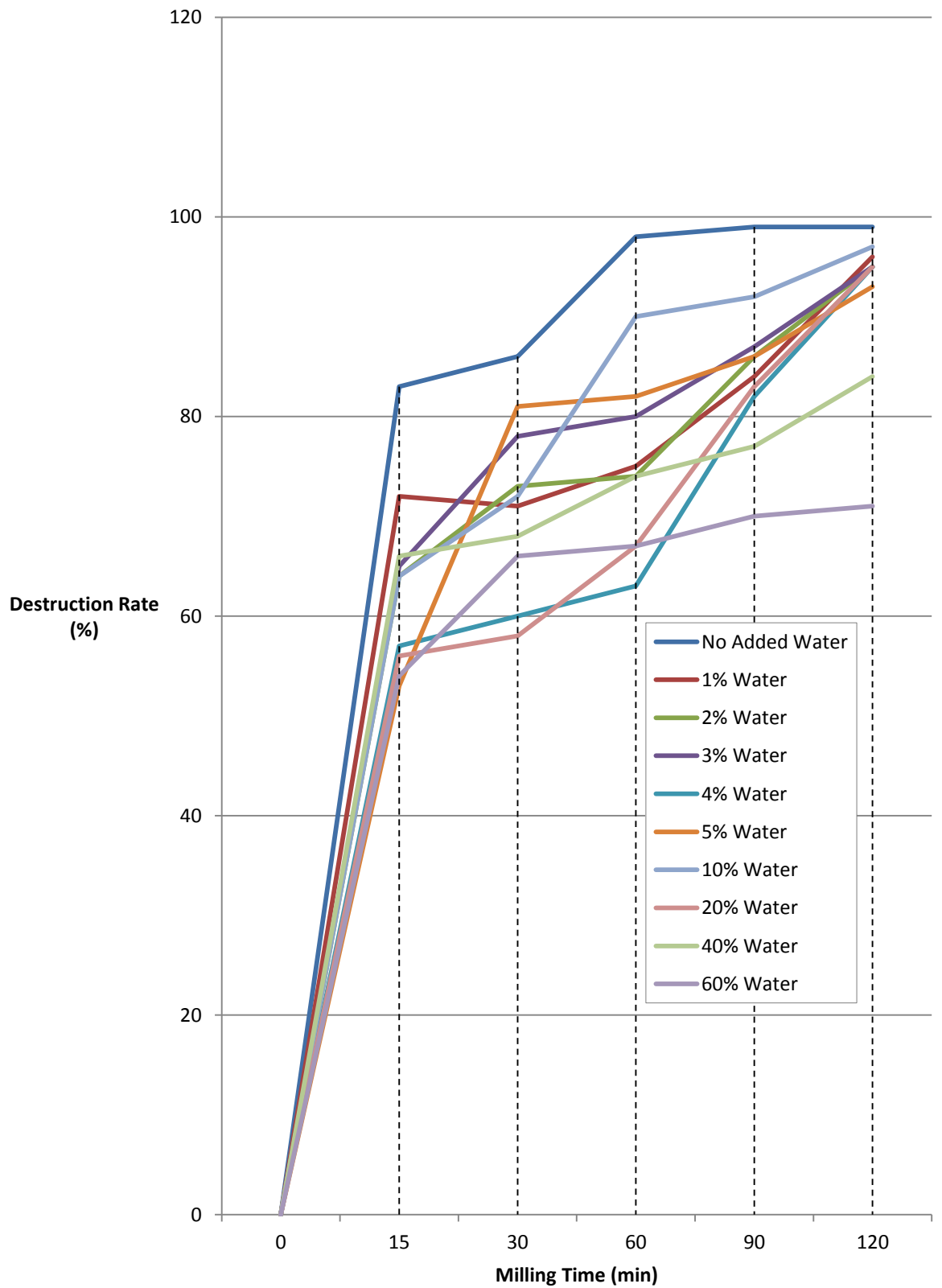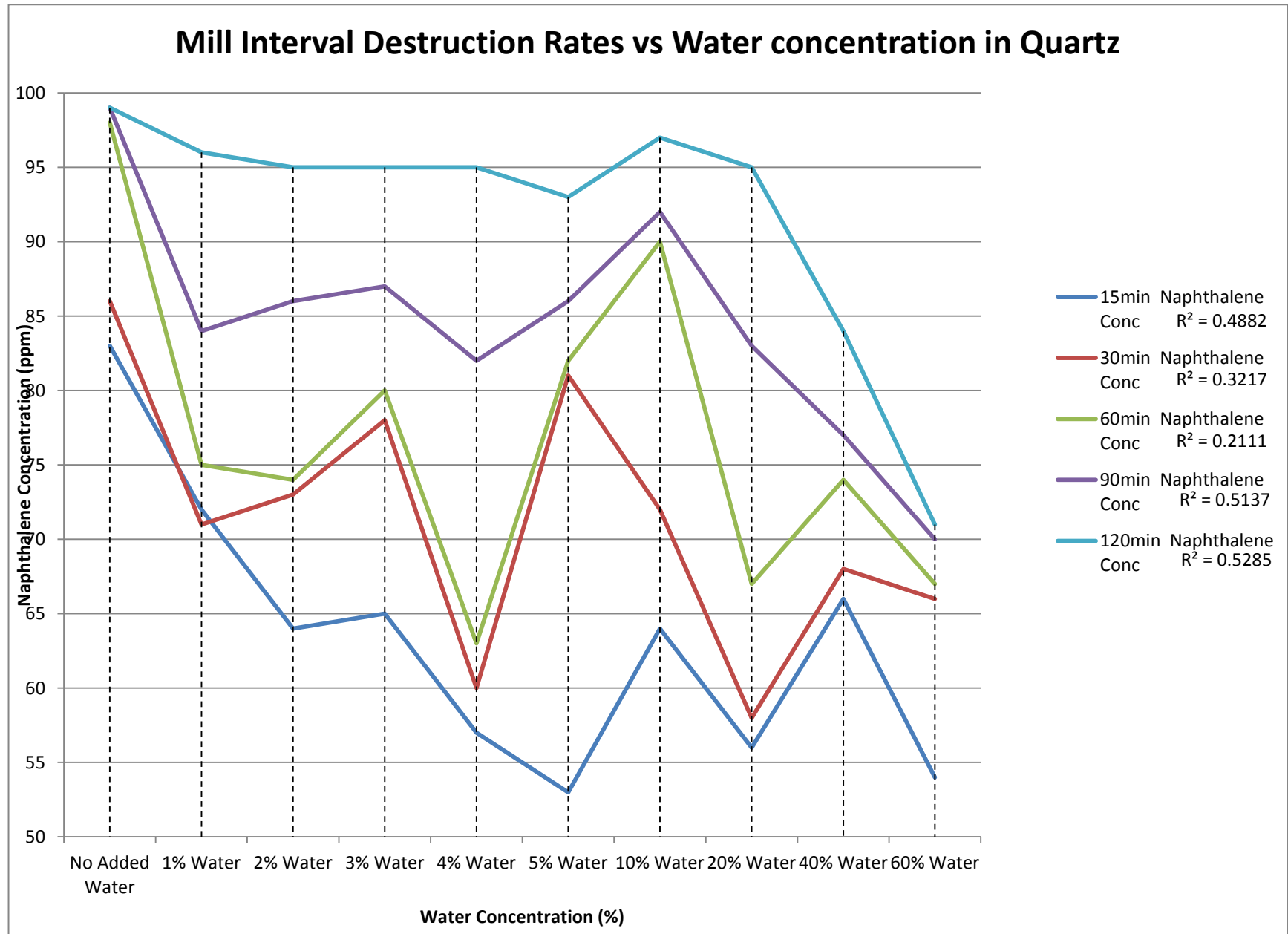
The mill speed was reduced from 500rpm to 350rpm in order to detect intermediates. This reduction of speed would also reduce the destruction rate of naphthalene.

The 60% water sample was the least effective test while the 0% water sample was the best. There is an overall trend of reduced destruction rates with increased water content. Water does reduce the destruction rates of naphthalene. It seems that only highly water saturated quartz-rich soils would pose a problem for mechanochemical remediation i.e. 40-60% water concentrations.

The mill jar temperature reached 100°C by the final milling interval which means that most of the added water was evaporated therefore the destruction rate increased.

There was no inversely proportional linear relationship between milling time interval and water concentration. The average linear regression coefficient of determination was $R^2 = 0.41$.

As mentioned before, the moisture trials were conducted at a milling speed of 350rpm in order to decrease the chances of destroying any intermediates generated. This was done to see what effect water has during milling and study its role as a radical scavenger.

Intermediates were only detected in the quartz moisture trials of 1%, 2%, 5% and 20% water concentrations. The intermediates generated during the quartz moisture trial were as follows:

Quartz 1% Water Intermediates

1,4-Naphthelenedione

1-Indanone

2H-Benzopyran-2-one

4-Hydroxy-1-naphthaldehyde

125

Quartz 2% Water Intermediates

2,2-diethyl-3-oxo-5-phenyl-4-pentenoate

Quartz 5% Water Intermediates

2-Naphthol

2H-1-Benzopyran-2-one

1-Naphthoic Acid

Quartz 20% Water Intermediates

4-Hydroxymethylester
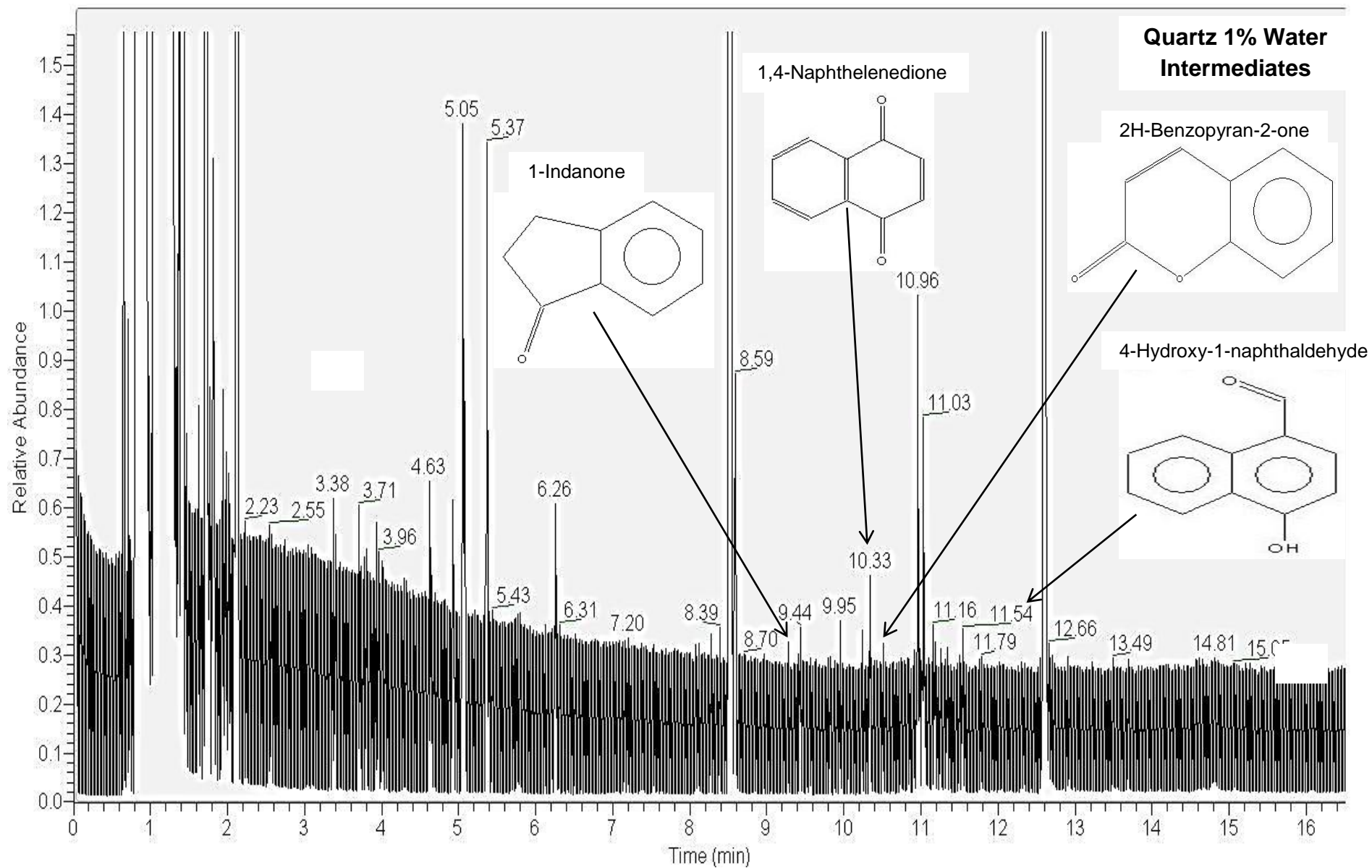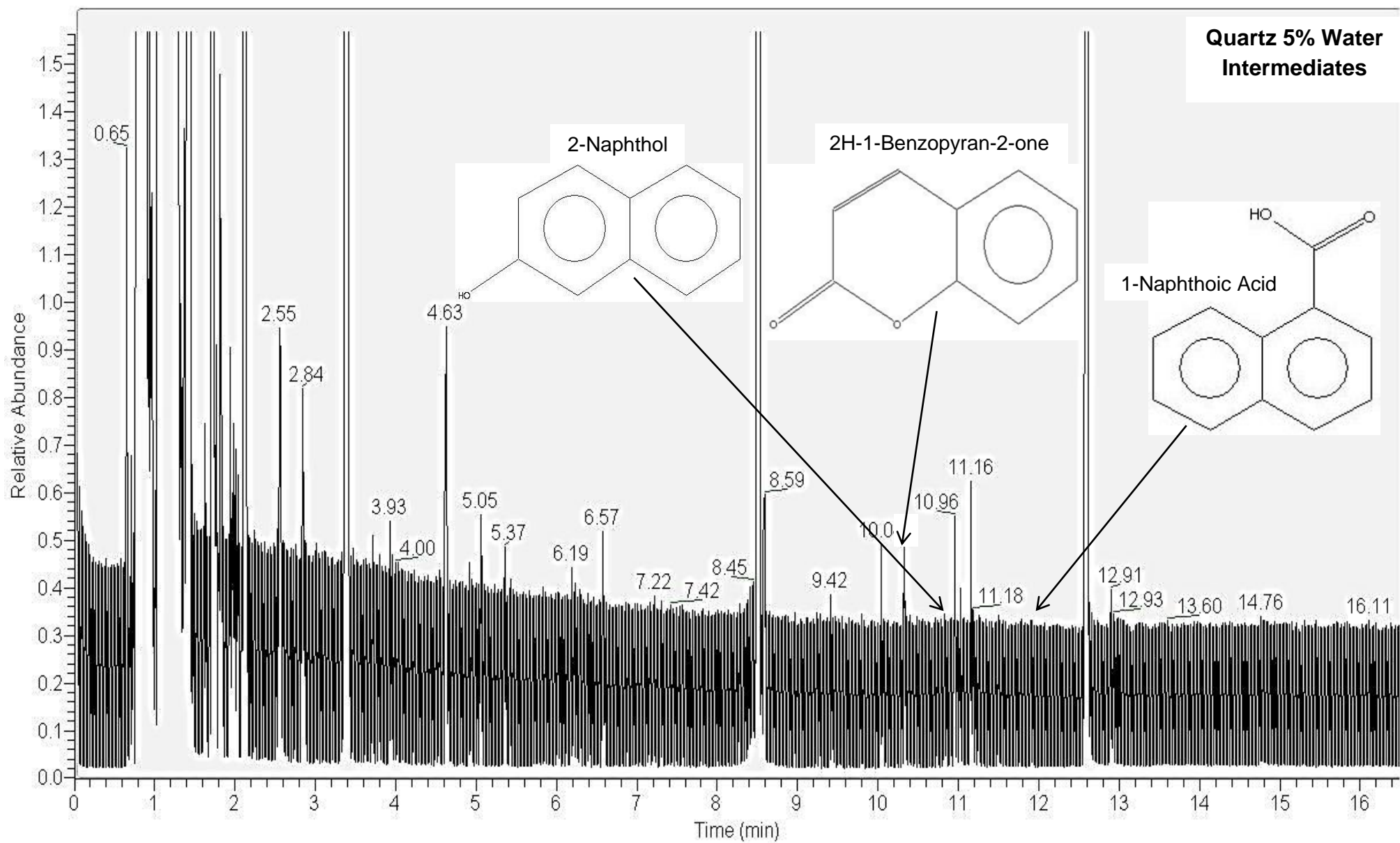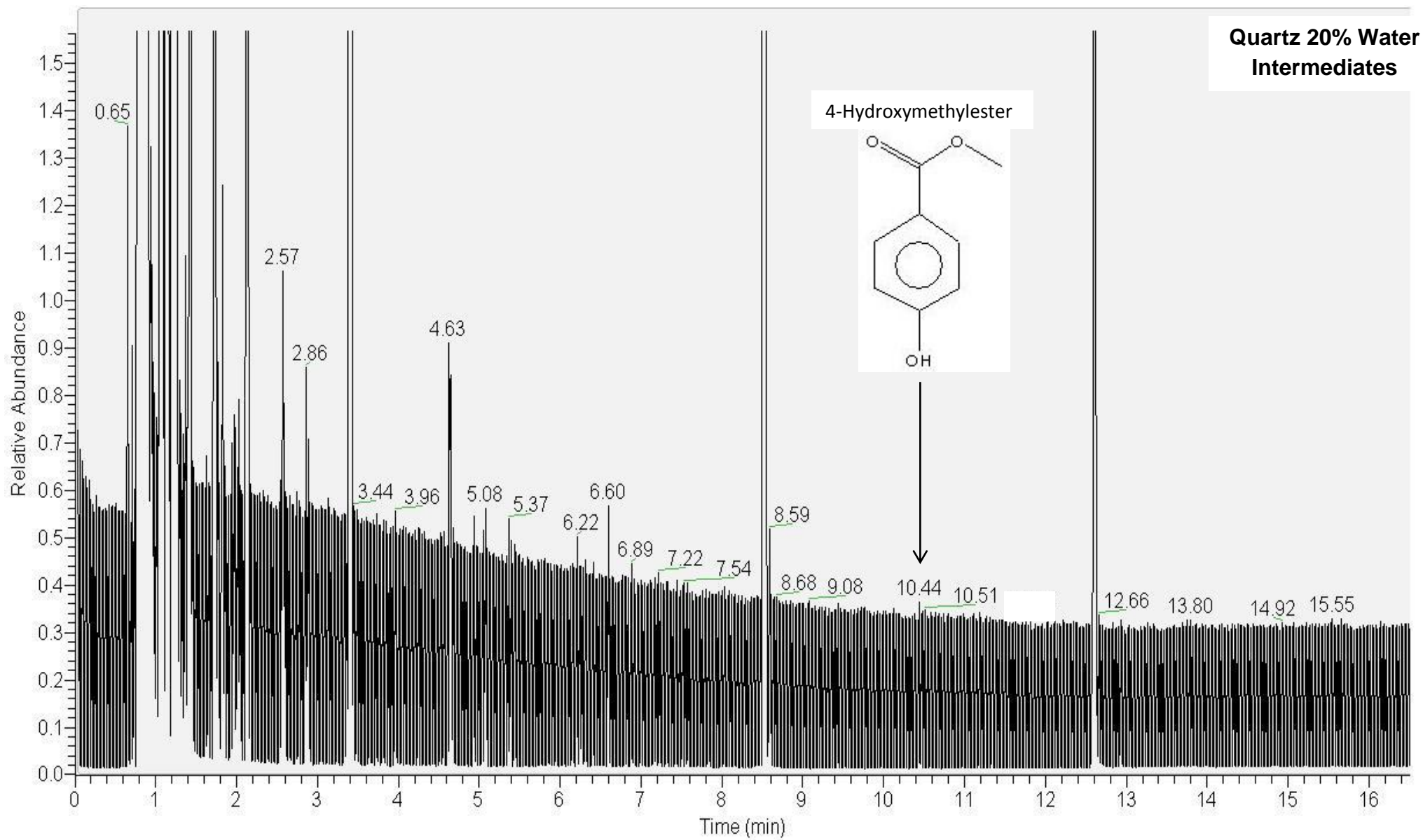
6.3.2 Scoria Moisture Trial

Three 50g samples of scoria were dried at 100°C overnight to remove all free water. Then two of the samples were moistened with water at concentrations of 2% and 5% by weight and one was left dry to serve as the control.

6.3.2.1 Scoria Dried at 100°C With No Added Water

Destruction Efficiency of Naphthalene in Scoria with 0% Water

Naphthalene Concentration (ppm) vs Milling Time (min)

- 15 min: 1869
- 30 min: 814
- 60 min: 389
- 90 min: 238
- 120 min: 150

6.3.2.2 Scoria 2% Water
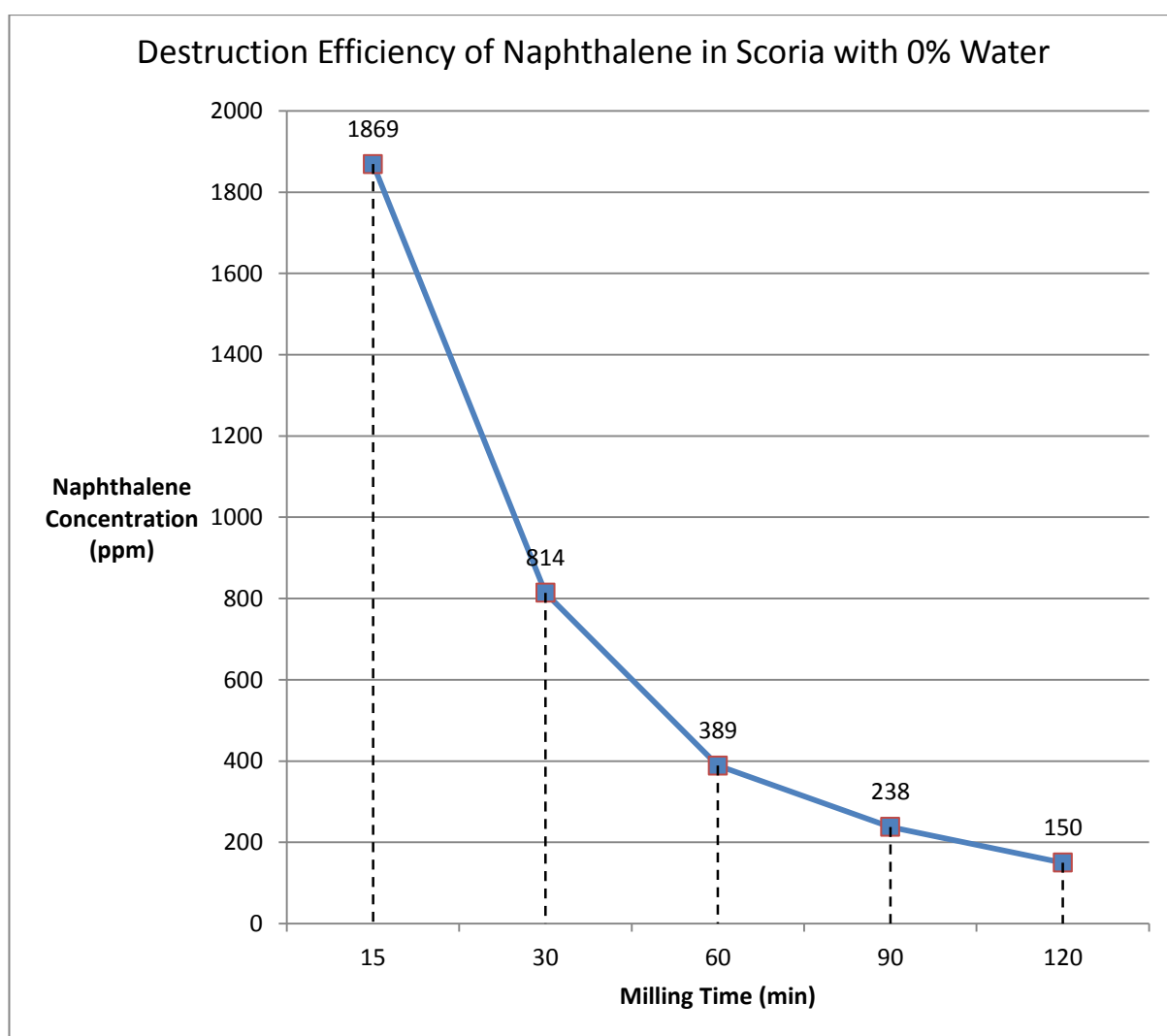
Destruction Efficiency of Naphthalene in Scoria with 2% Water

6.3.2.3 Scoria 5% Water
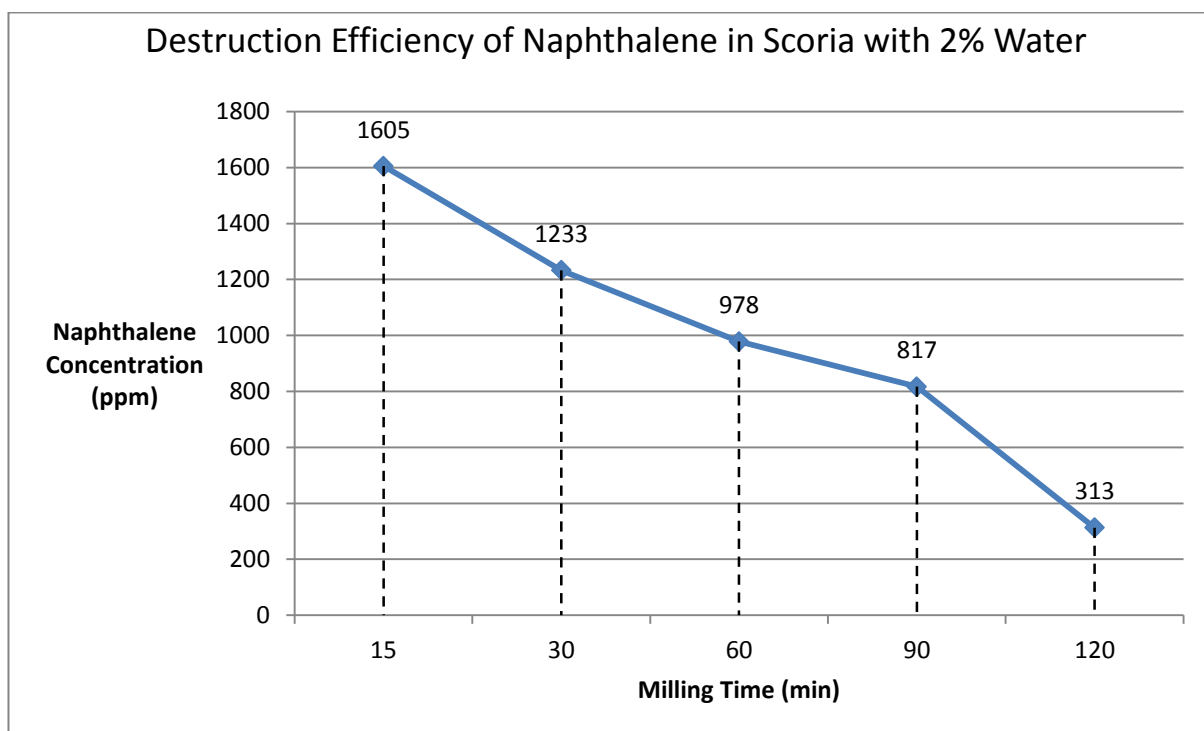
Destruction Efficiency of Naphthalene in Scoria with 5% Water

6.3.2.3 Discussion

Milling Interval (min)	No Added Water Naphthalene Conc. (ppm)	No Added Water Destruction Rate (%)
0	5000	0
15	1869	63
30	814	84
60	389	92
90	238	95
120	150	97

Milling Interval (min)	2% Water Naphthalene Conc. (ppm)	2% Water Destruction Rate (%)
0	5000	0
15	1605	68
30	1233	75
60	978	80
90	817	84
120	313	94

Milling Interval (min)	5% Water Naphthalene Conc. (ppm)	5% Water Destruction Rate (%)
0	5000	0
15	2226	55
30	1826	63
60	1702	66
90	1516	70
120	1497	70

Destruction Efficiency of Naphthalene vs Water Content
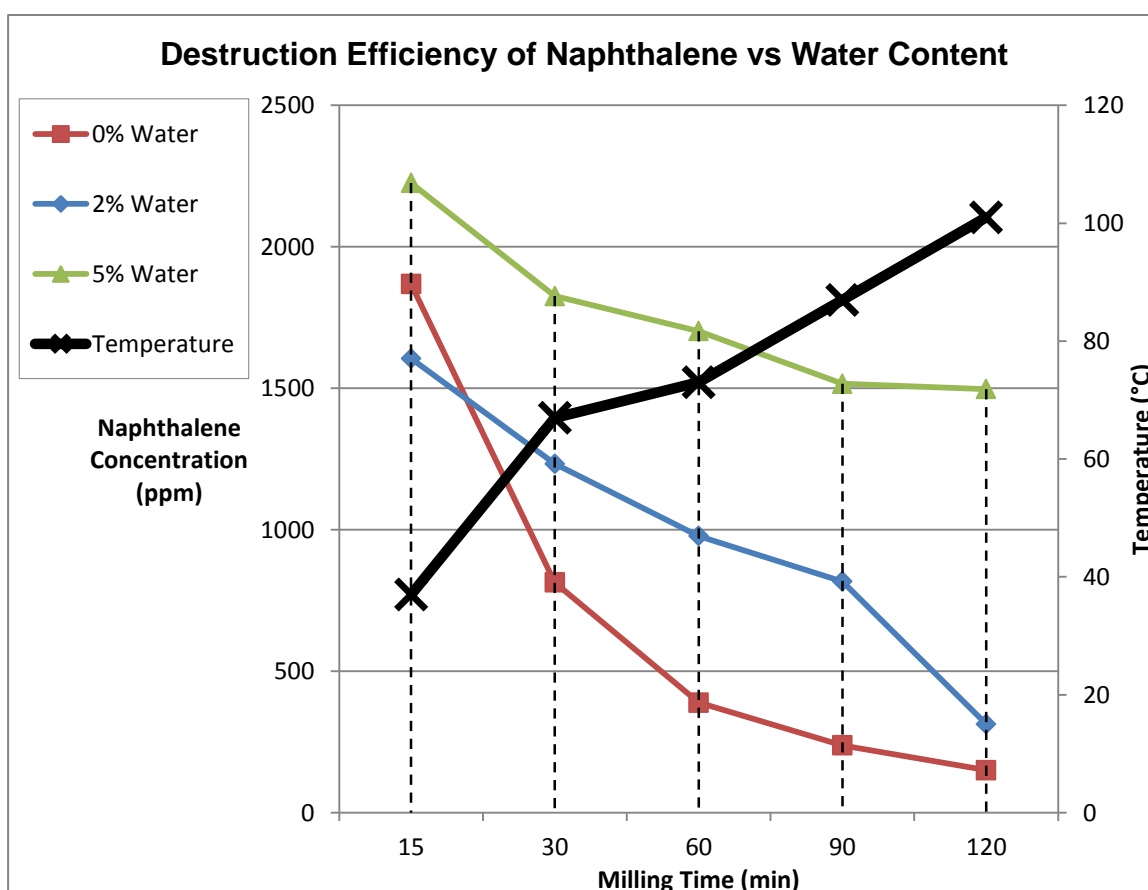
Naphthalene Destruction Rates in Scoria at Different Water Concentrations

Mill Interval Destruction Rates vs Water concentration in Scoria

Legend:
- 15min Naphthalene Conc — $R^2 = 0.3721$
- 30min Naphthalene Conc — $R^2 = 0.9932$
- 60min Naphthalene Conc — $R^2 = 0.998$
- 90min Naphthalene Conc — $R^2 = 0.9952$
- 120min Naphthalene Conc — $R^2 = 0.8322$

X-axis: Water Concentration (%) — No Added Water, 2% Water, 5% Water
Y-axis: Naphthalene Concentration (ppm)
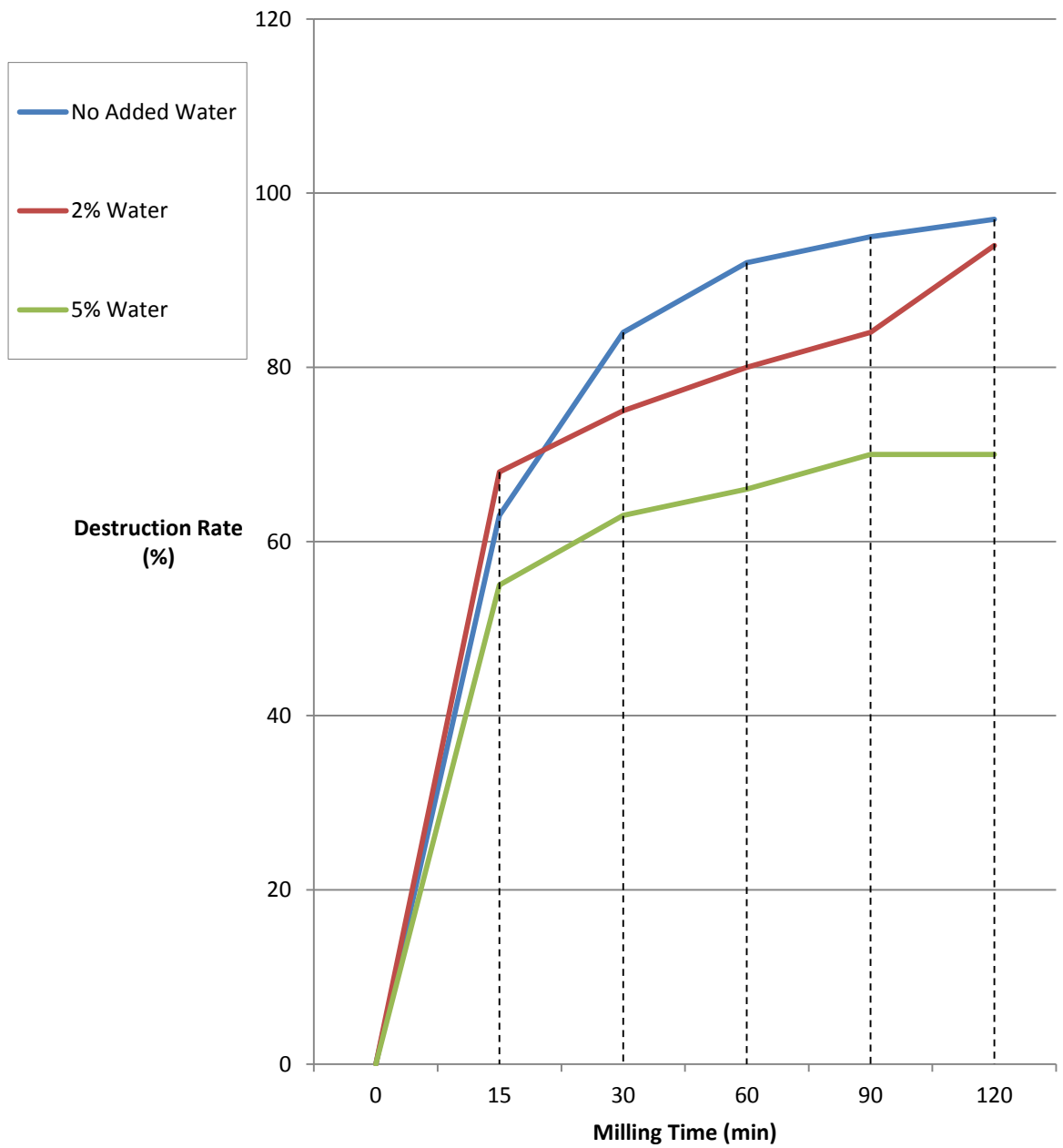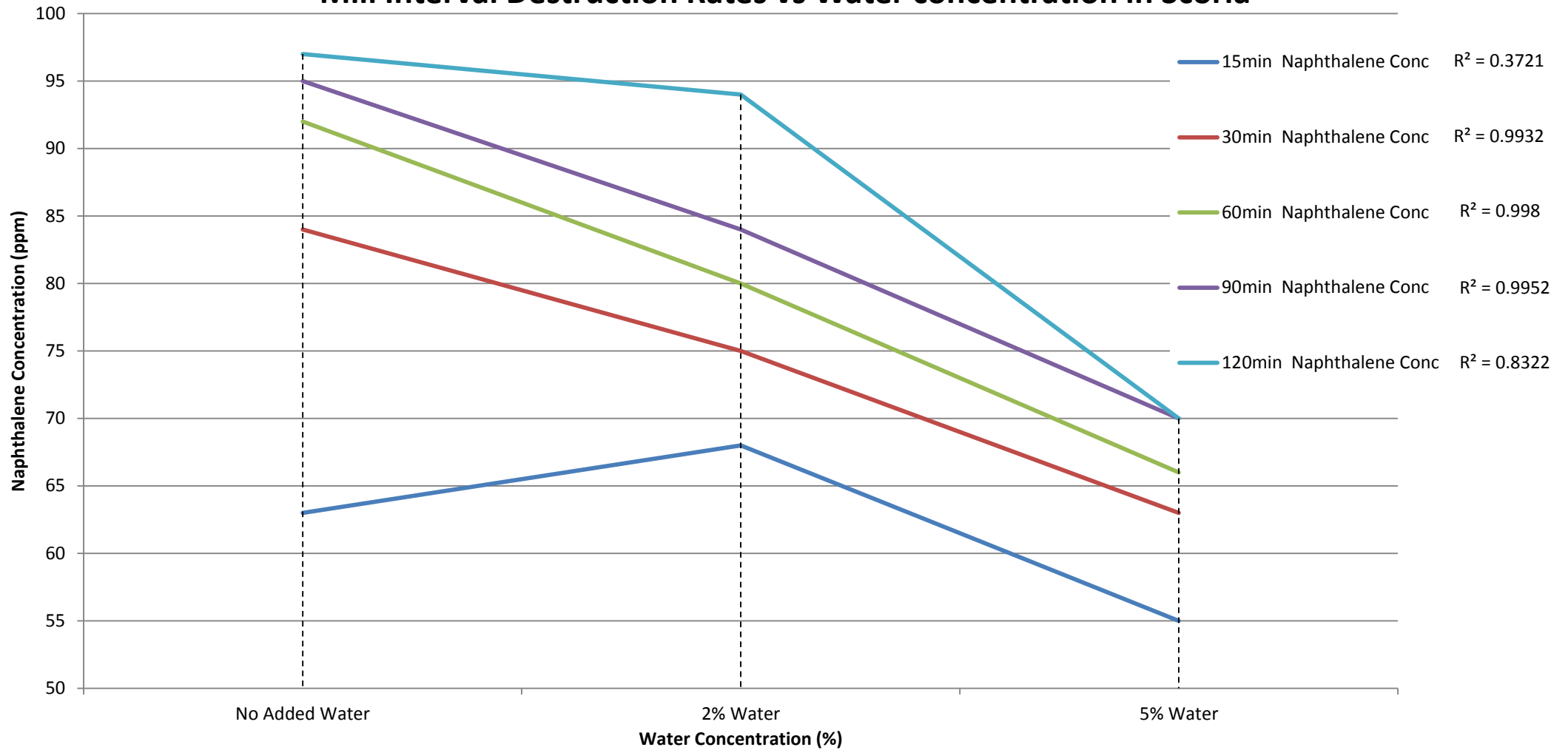
The behaviour of Scoria with water resulted in a decrease of naphthalene destruction as water concentration increased. At 5% water concentration, there seems to be a plateau developing by the 90 minute milling interval. Both interval 90 and 120 minute had destruction rates of 70%. This mirrored the quartz moisture trial results.

Another attempt was made to find an inverse linear relationship between milling time interval and water concentration. This time, three milling intervals did exhibit inverse proportionality; 30, 60 and 90 minutes. The linear regression coefficients of determination were 0.993, 0.998 and 0.995 respectively.

A search for water induced intermediates was carried out and was detected in both the 2% and 5% water concentration samples and they were as follows:

Scoria 2% Water Intermediates

4-Ethoxy-3-hydroxybenzaldehyde

1-Indanone

Benzothiophene-1-dioxide

1-Naphthol

Scoria 5% Water Intermediates
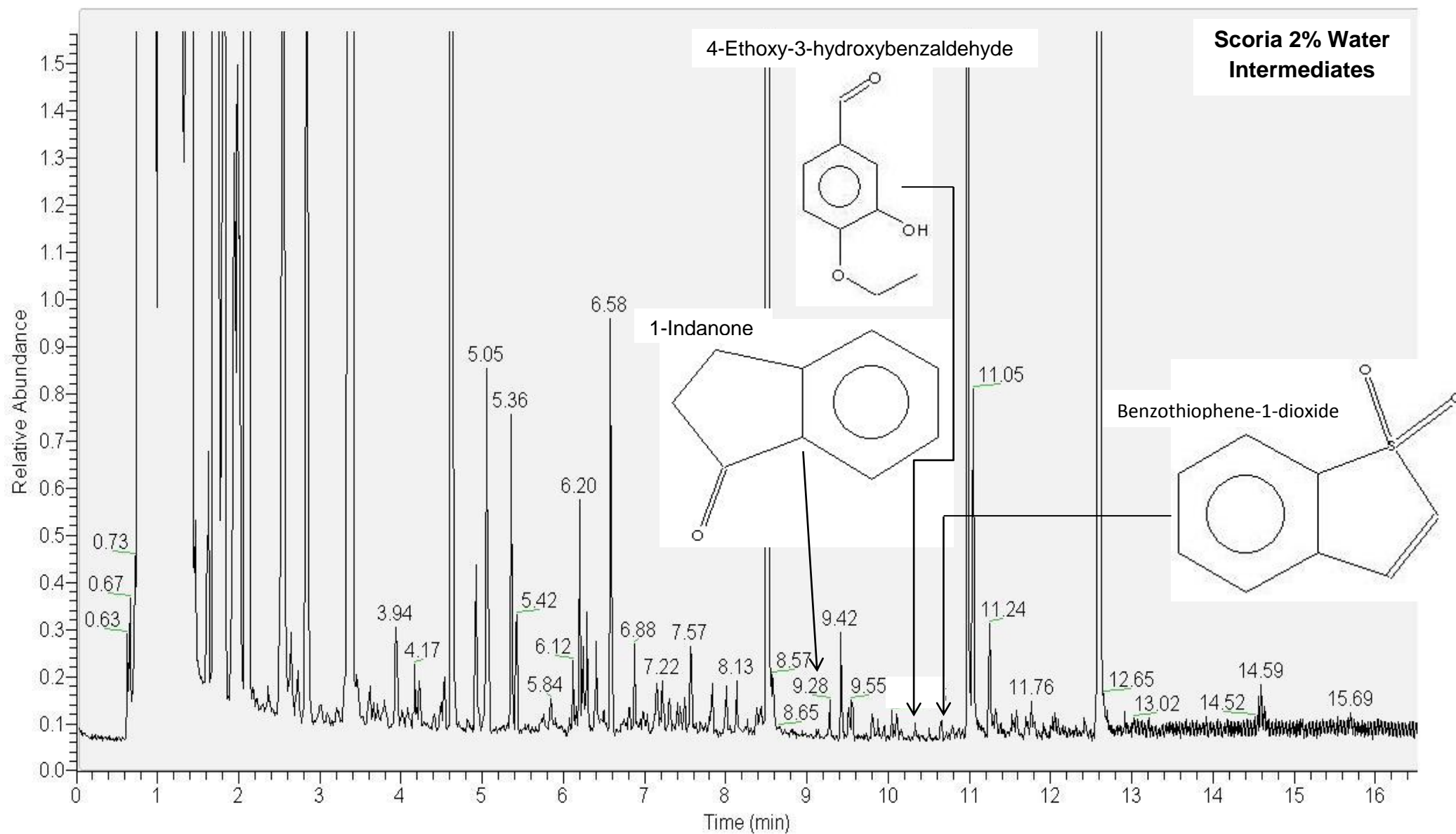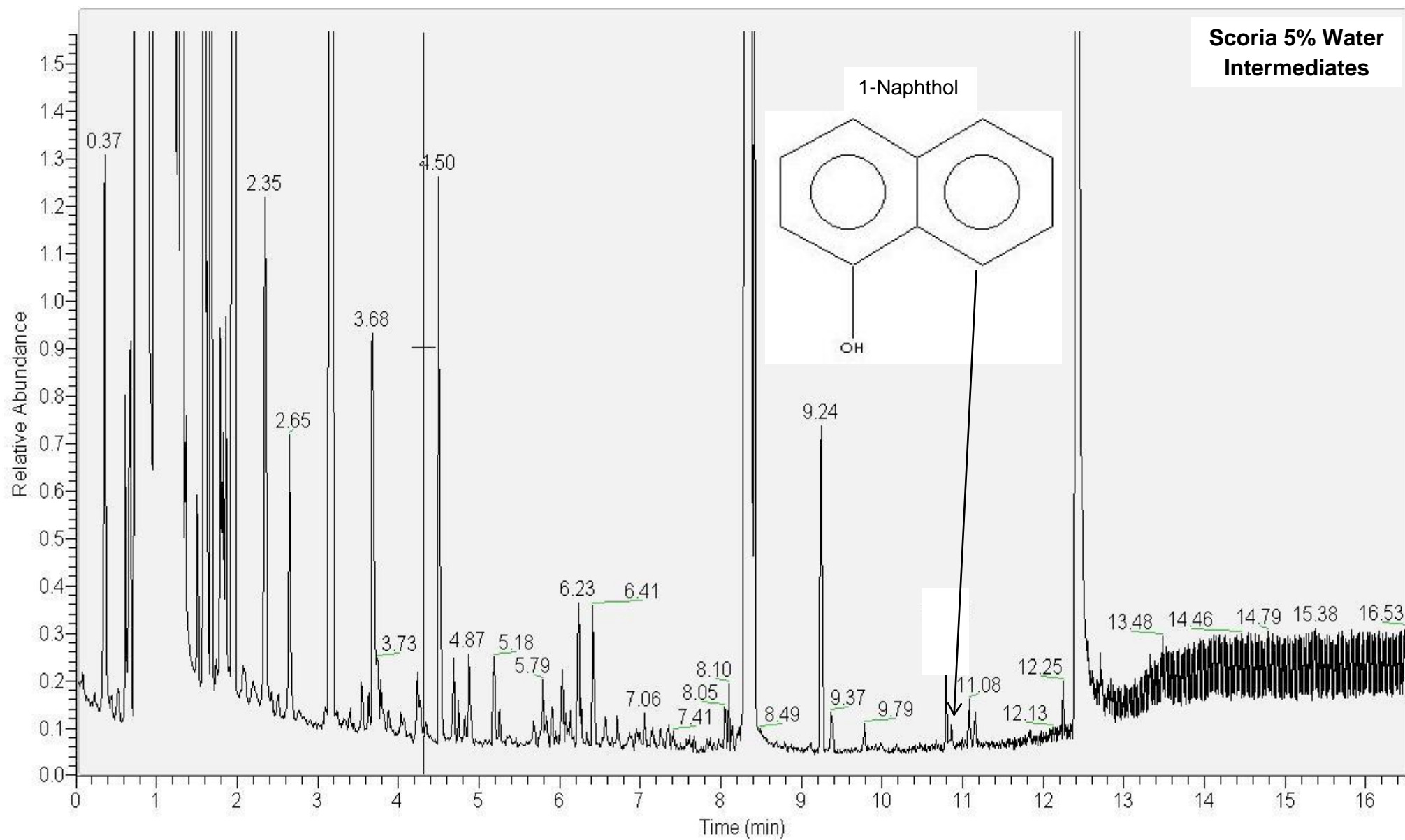
6.3.3 Limestone Moisture Trial

Four 50g samples of limestone were dried at 100°C overnight to remove all free water. Then three of the samples were moistened with water at concentrations of 2%, 5% and 10% by weight and one was left dry to serve as the control.

6.3.3.1 Limestone at 100°C with No Added Water

Destruction Efficiency of Naphthalene in Limestone with 0% Water

6.3.3.2 Limestone 2% Water
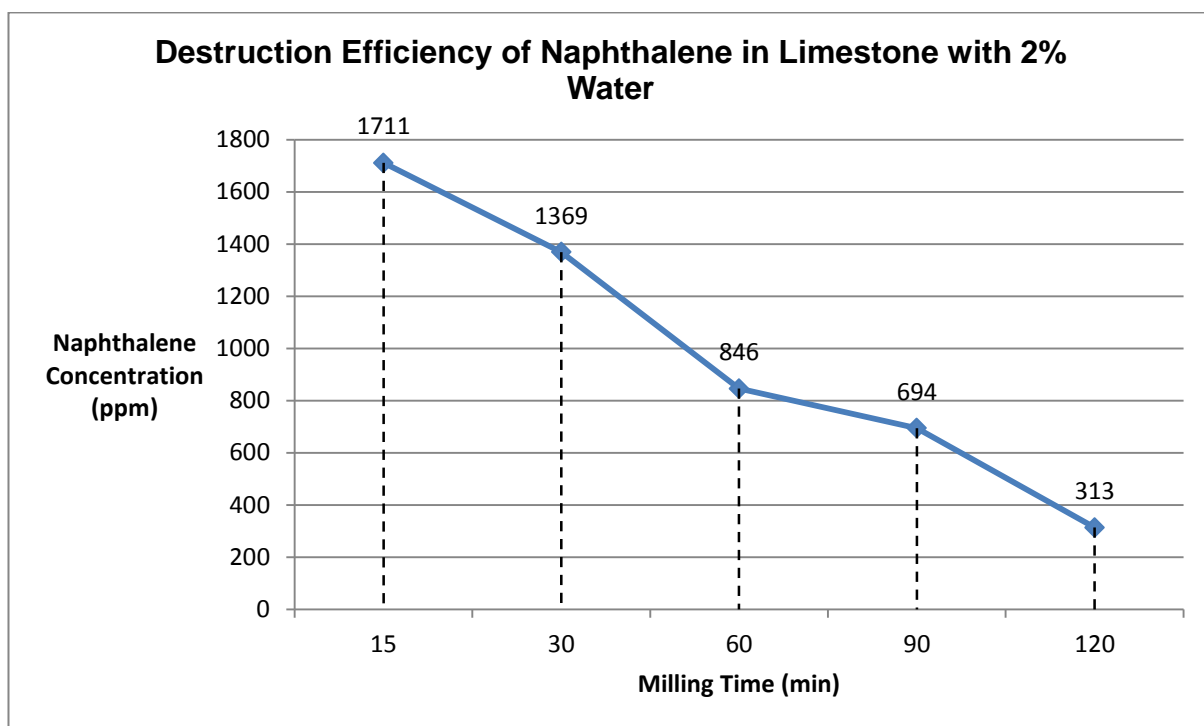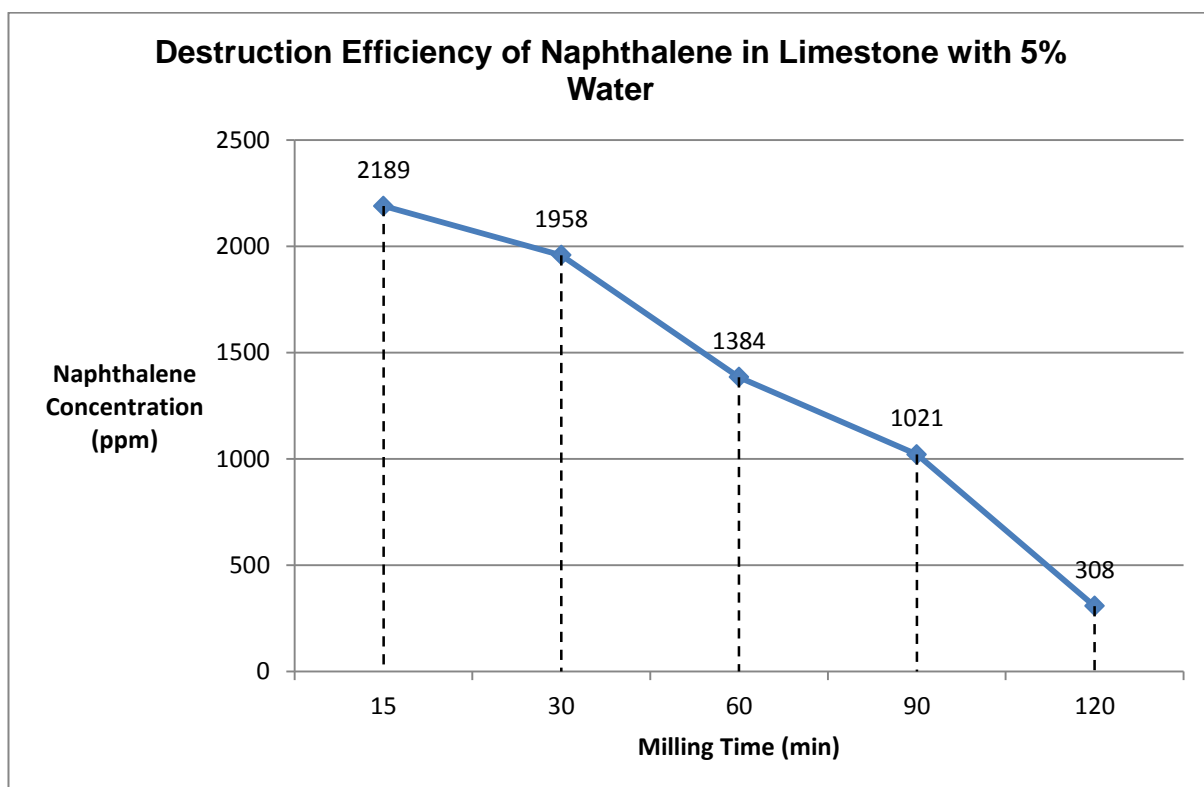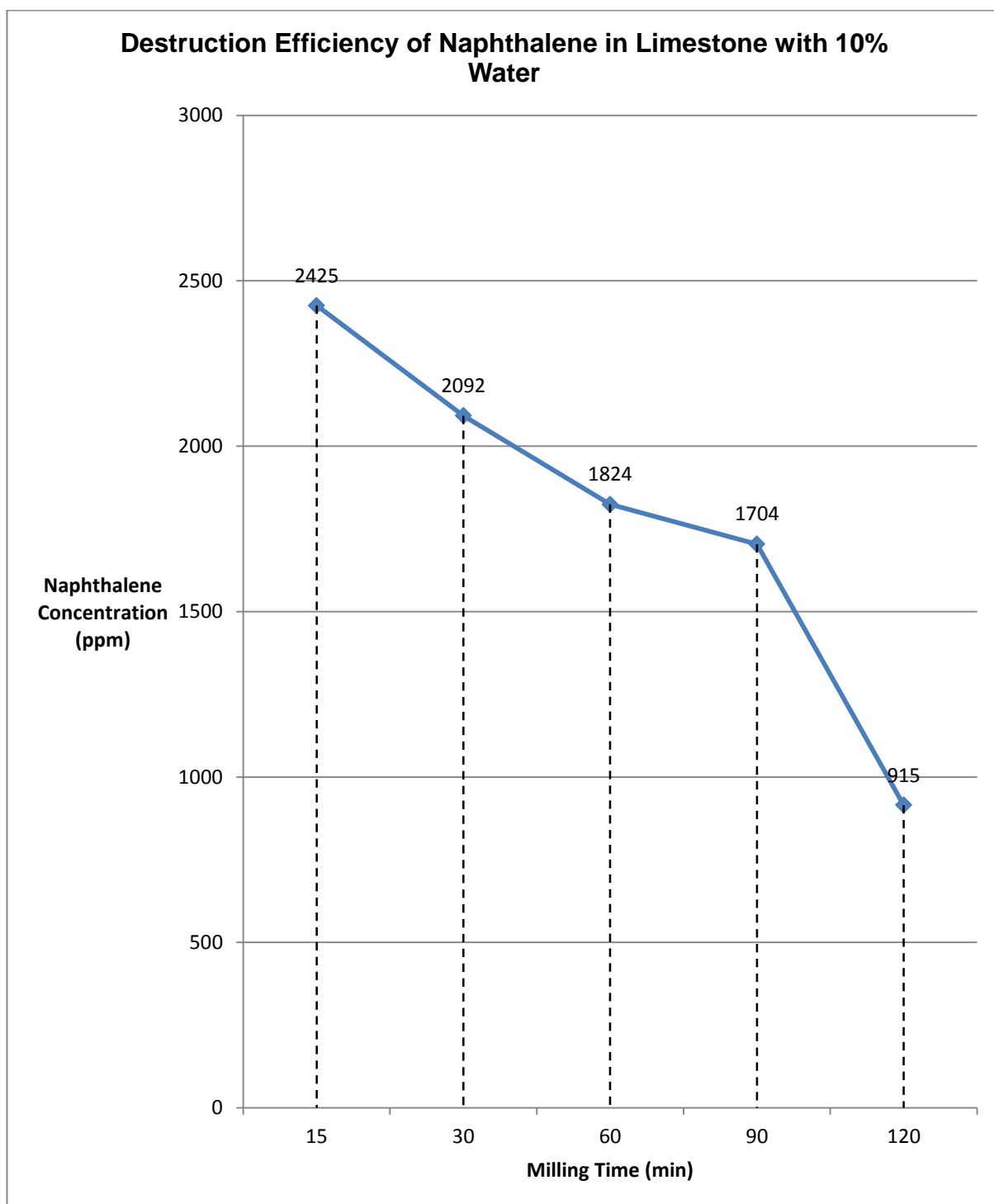
Destruction Efficiency of Naphthalene in Limestone with 2% Water

Naphthalene Concentration (ppm)

- 1711
- 1369
- 846
- 694
- 313

Milling Time (min): 15, 30, 60, 90, 120

6.3.3.3 Limestone 5% Water

Destruction Efficiency of Naphthalene in Limestone with 5% Water

Naphthalene Concentration (ppm)

- 2189
- 1958
- 1384
- 1021
- 308

Milling Time (min): 15, 30, 60, 90, 120

6.3.3.4 Limestone 10% Water

Destruction Efficiency of Naphthalene in Limestone with 10% Water

Naphthalene Concentration (ppm) vs Milling Time (min)

2425, 2092, 1824, 1704, 915

6.3.3.5 Discussion

Milling Interval (min)	No Added Water Naphthalene Conc. (ppm)	No Added Water Destruction Rate (%)
0	5000	0
15	1170	77
30	979	80
60	543	89
90	414	92
120	234	95

Milling Interval (min)	2% Water Naphthalene Conc. (ppm)	1% Water Destruction Rate (%)
0	5000	0
15	1711	66
30	1369	73
60	846	83
90	694	86
120	313	94

Milling Interval (min)	5% Water Naphthalene Conc. (ppm)	5% Water Destruction Rate (%)
0	5000	0
15	2189	56
30	1958	61
60	1384	72
90	1021	80
120	308	94

Milling Interval (min)	10% Water Naphthalene Conc. (ppm)	10% Water Destruction Rate (%)
0	5000	0
15	2425	52
30	2092	58
60	1824	64
90	1704	66
120	915	82

Naphthalene Abundance in Limestone vs Water Content

Naphthalene Destruction Rate in Limestone with Different Water Concentrations
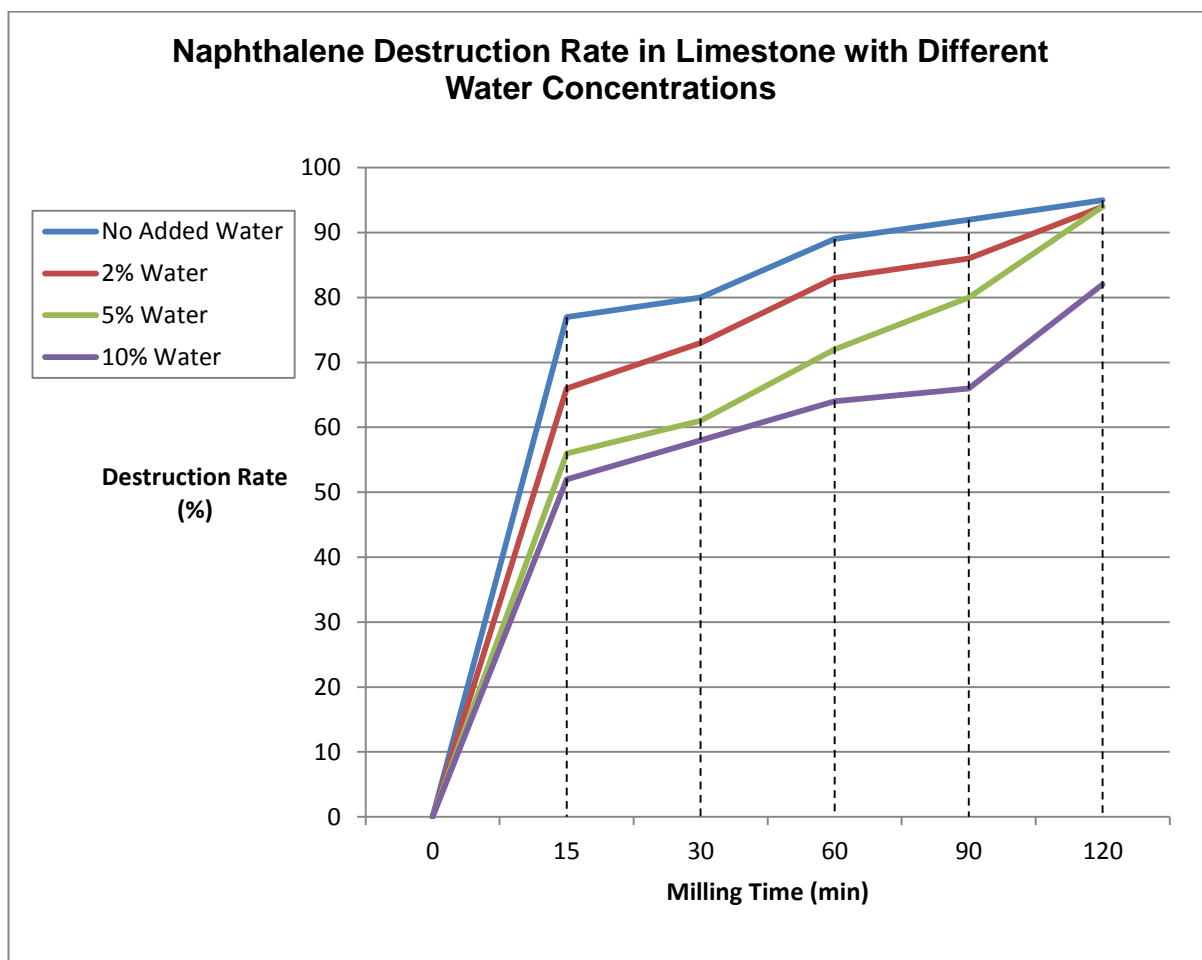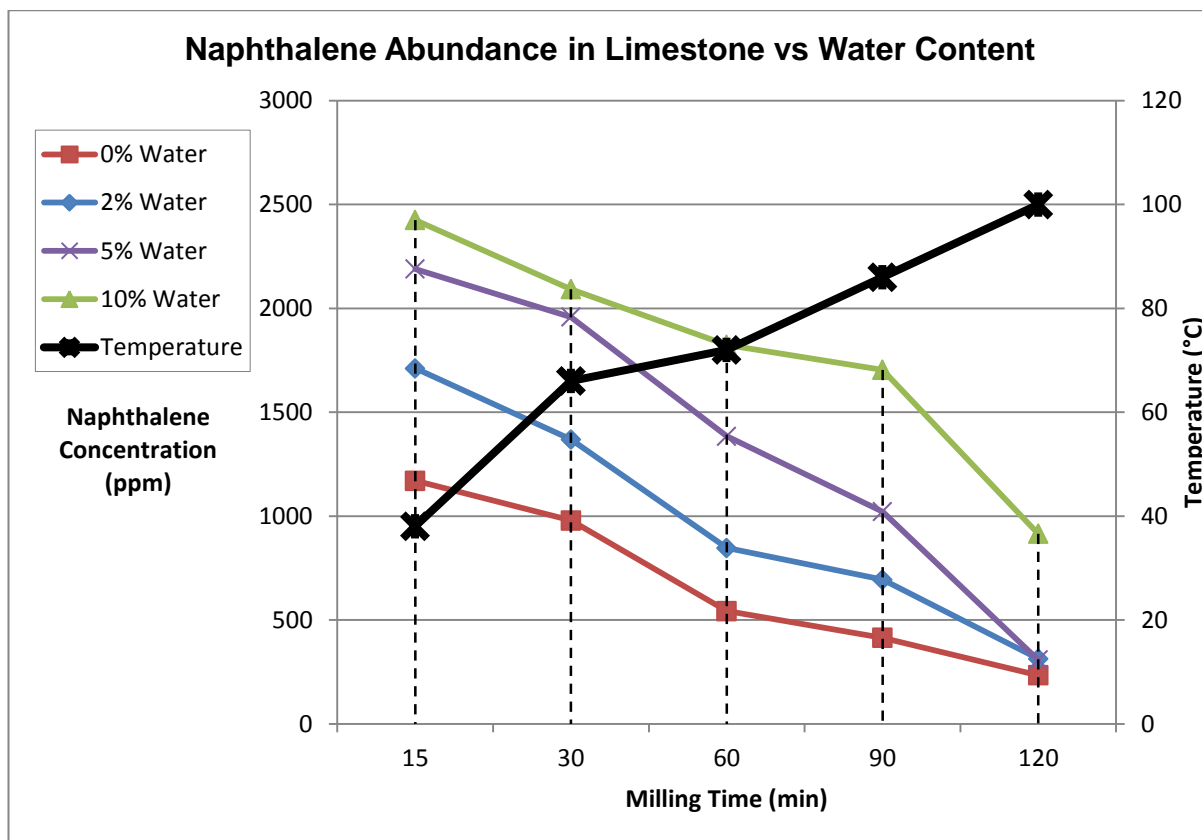
Mill Interval Destruction Rates vs Water concentration in Limestone
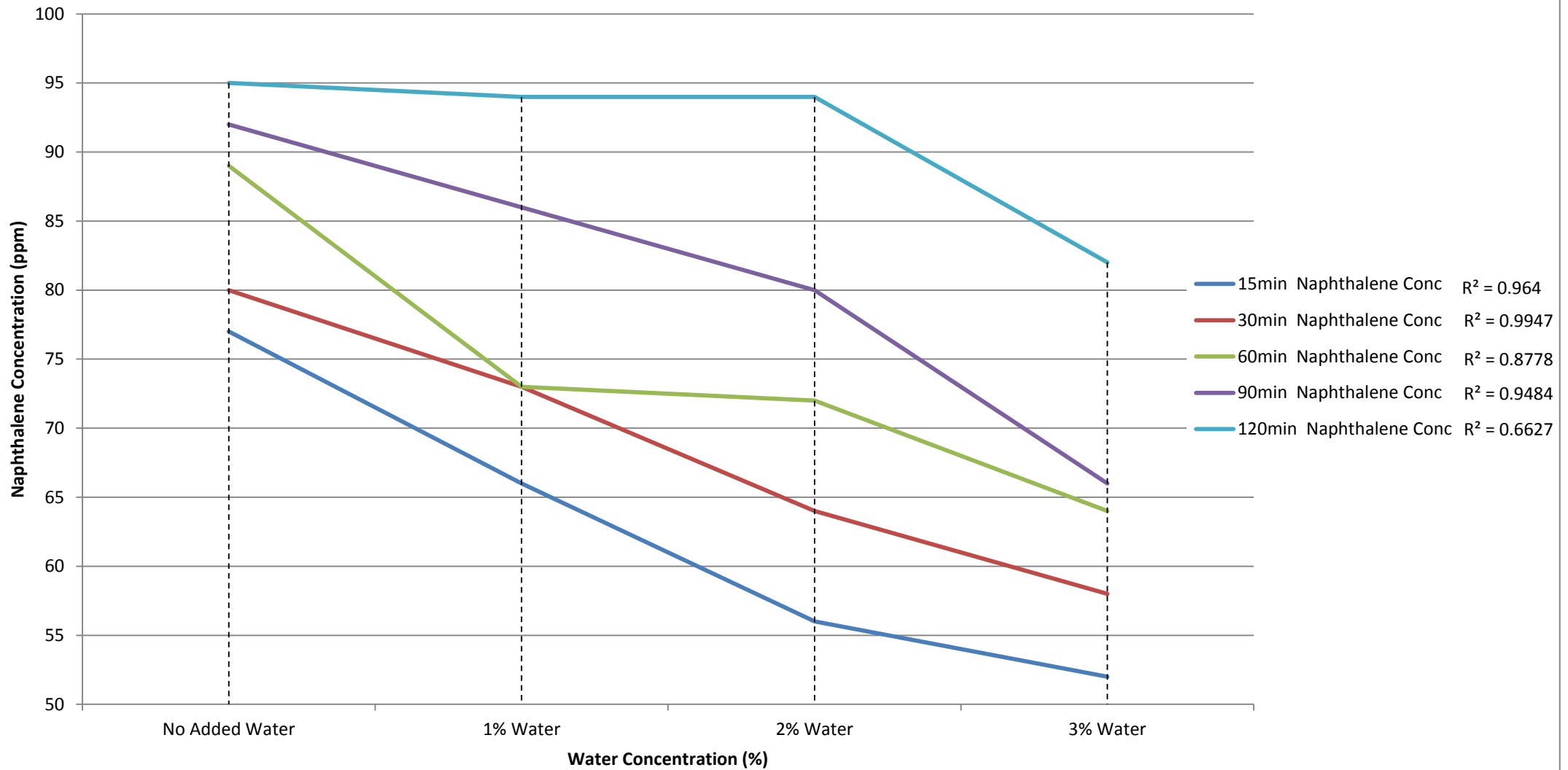
The limestone moisture trial results followed the same trends as the previous soils. Naphthalene destruction rates decreased as water concentrations increased. The 5% and 10% water trials both experienced a relatively sharp increase in naphthalene destruction rates during the 120 minute milling interval. This increase coincided with a milling jar temperature of 101°C which indicates that some of the added water was lost via evaporation. Therefore, the destruction rates increased as the water concentration in the limestone decreased.

There was only one data set in the milling time interval versus water concentration that exhibited inverse proportionality, 30 minute milling interval. It had a linear regression coefficient of determination of $R^2 = 0.995$. Milling intervals of 15 and 90 minutes had linear regression coefficients of determination of 0.964 and 0.948 respectively; however this is not enough to be classified as linear.

Searches for water induced intermediates were carried out and detected in the 2%, 5% and 10% water concentration samples and they were as follows:

Vinyl(2E)-3-phenyl-2-propenoate

1-Naphthol

Limestone 2% Water

144

Limestone 5% Water

Vinyl(2E)-3-phenyl-2-propenoate

1-Naphthol

Limestone 10% Water

1-Naphthol
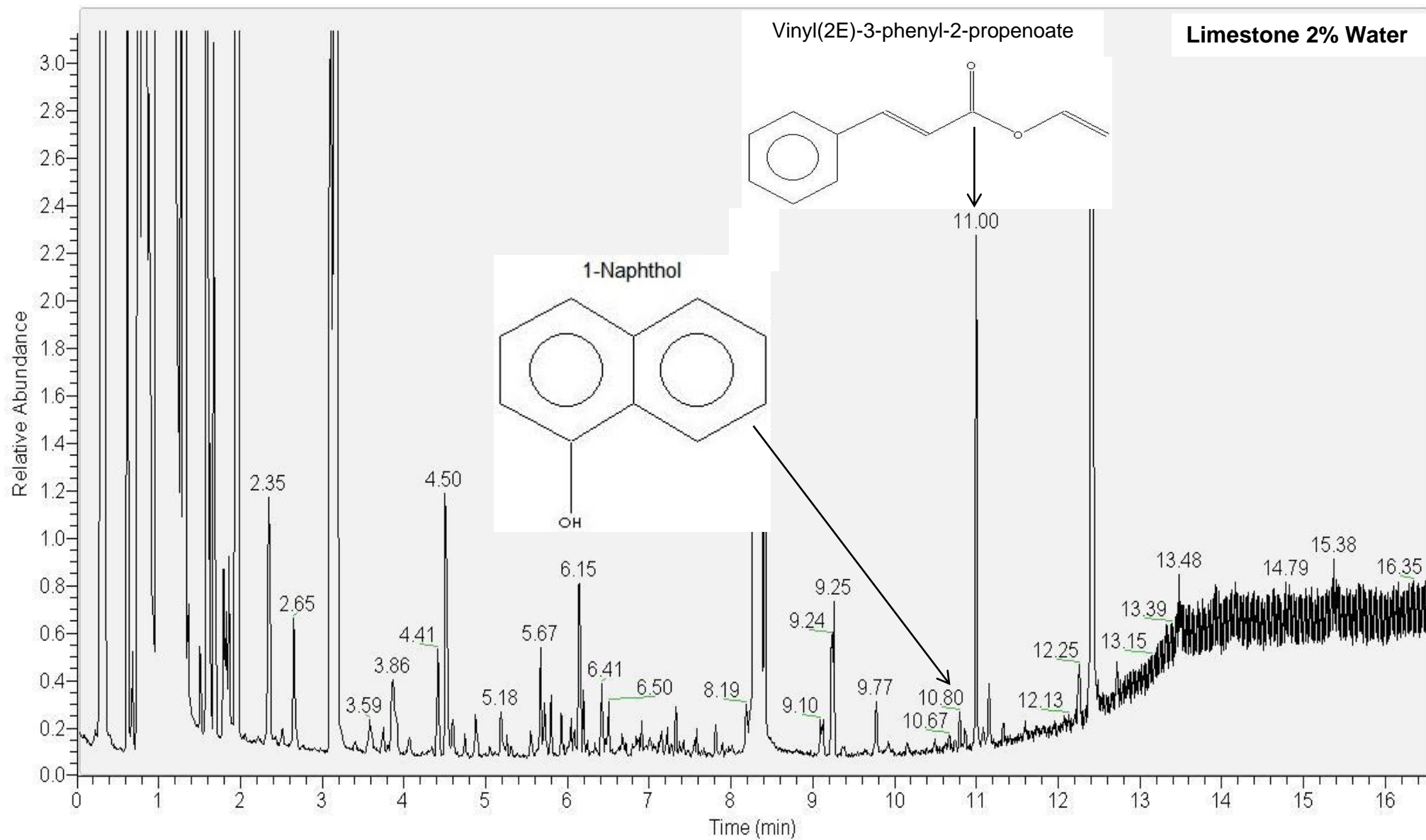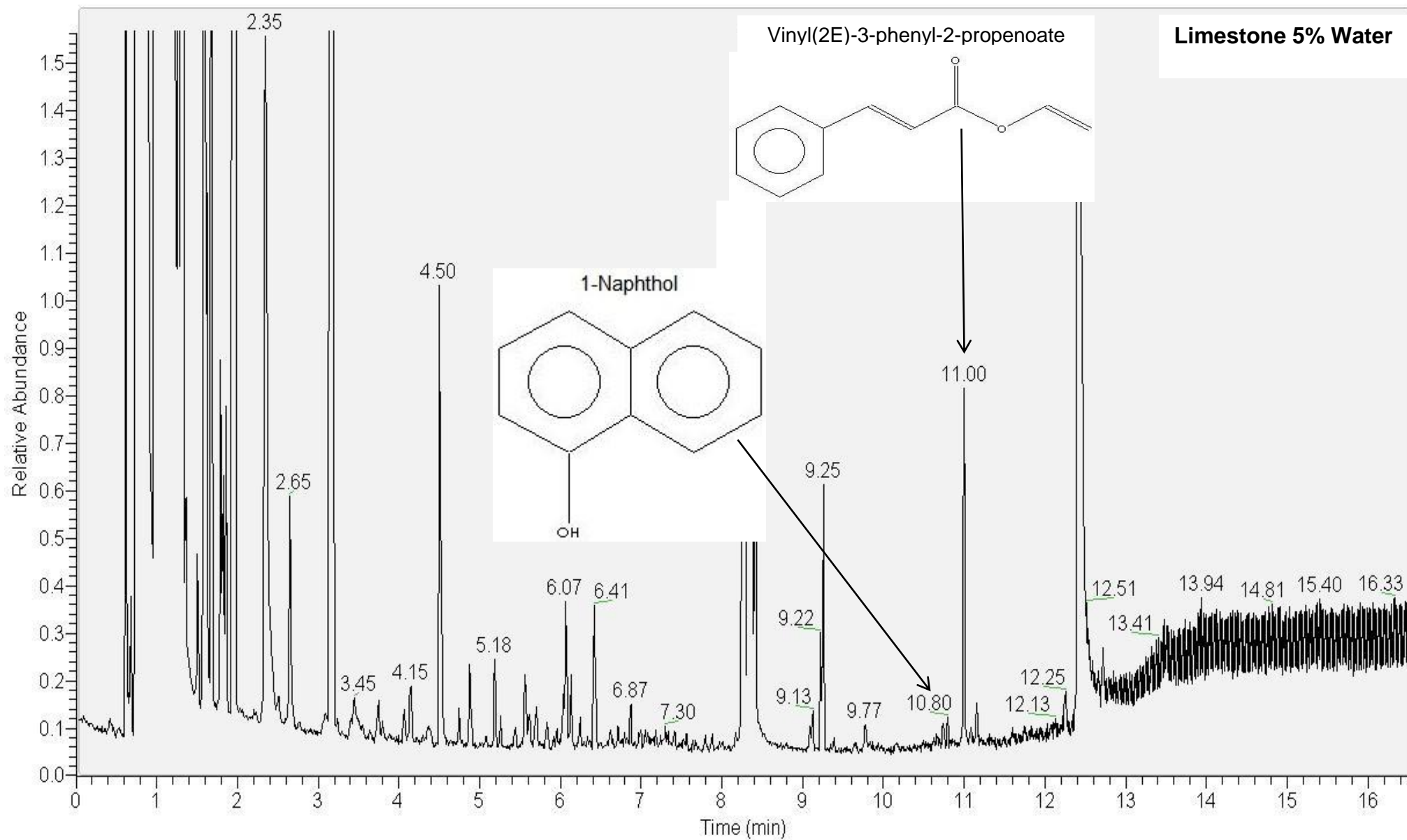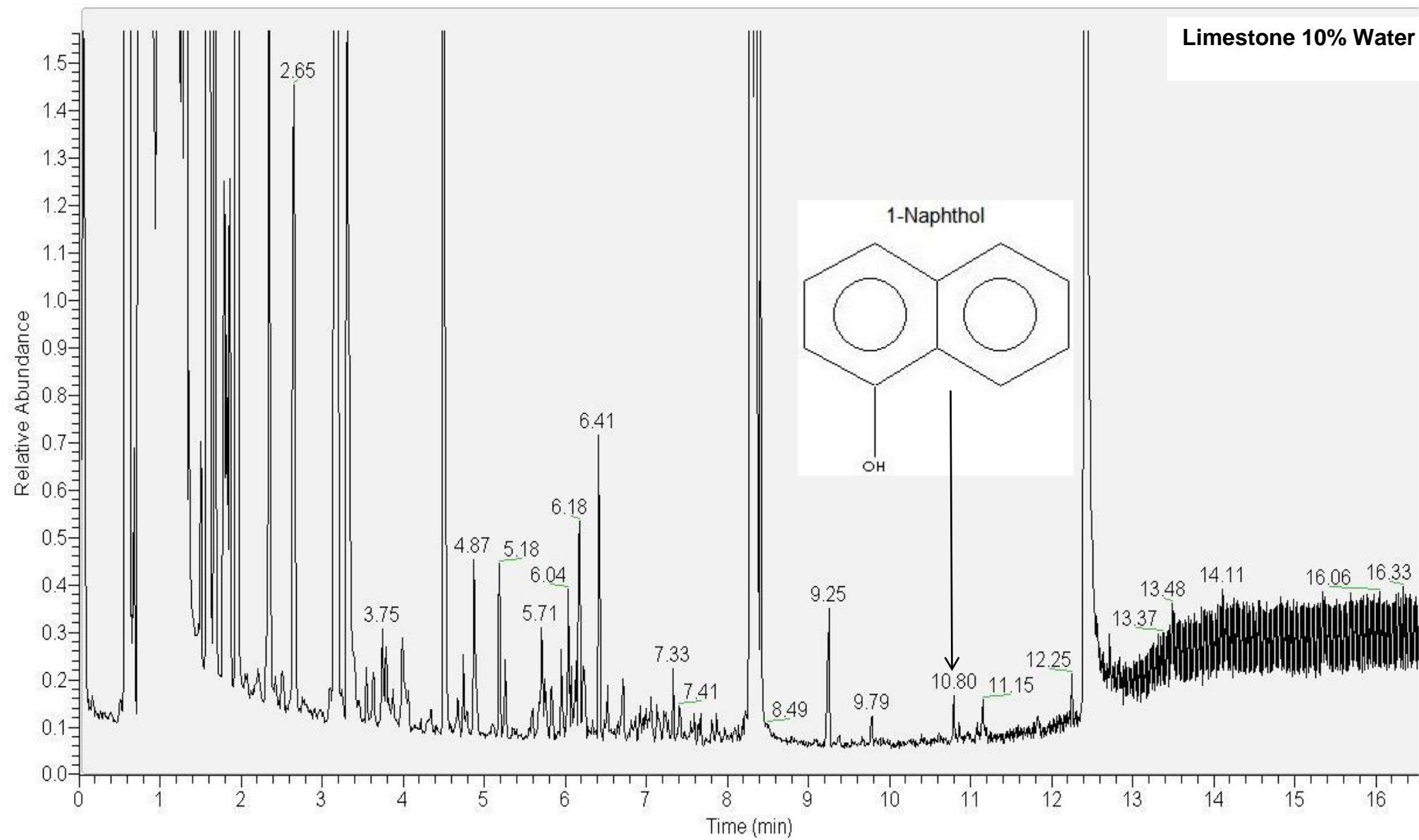
6.3.4 Sub Soil Moisture Trial

Four 50g samples of sub soil were dried at 100°C overnight to remove all free water. Then three of the samples were moistened with water at concentrations of 2%, 5% and 10% by weight and one was left dry to serve as the control.

6.3.4.1 Sub Soil Dried at 100°C With No Added Water.

Destruction Efficiency of Naphthalene in Sub Soil with 0% Water
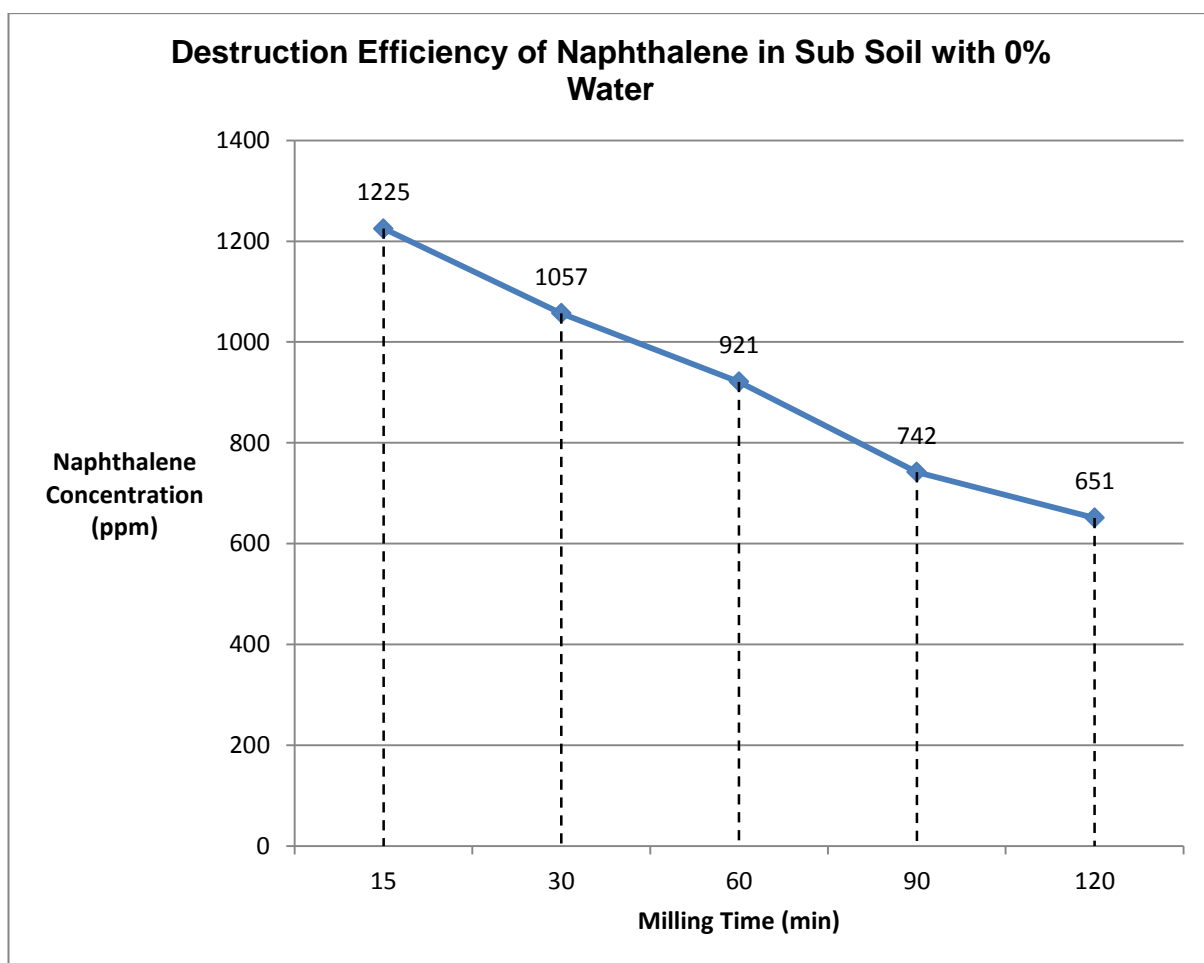
6.3.4.2 Sub Soil 2% Added Water

Destruction Efficiency of Naphthalene in Sub Soil with 2% Water

6.3.4.3 Sub Soil 5% Water
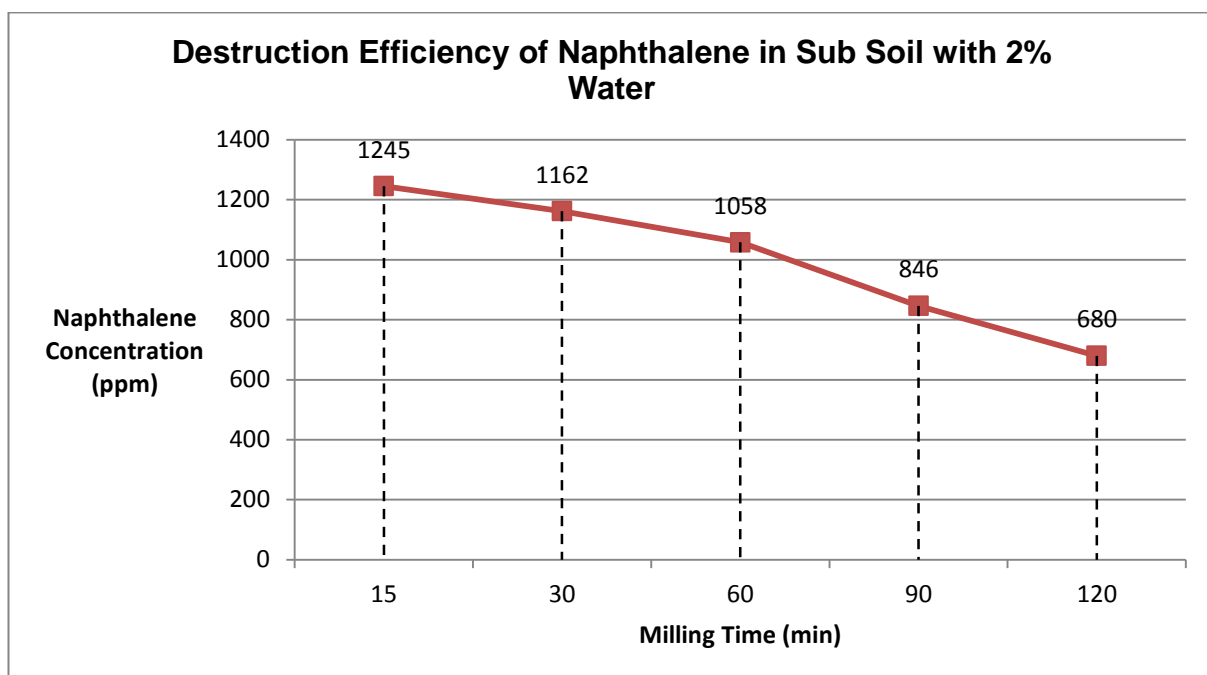
Destruction Efficiency of Naphthalene in Sub Soil with 5% Water

6.3.4.4 Sub Soil 10% Water
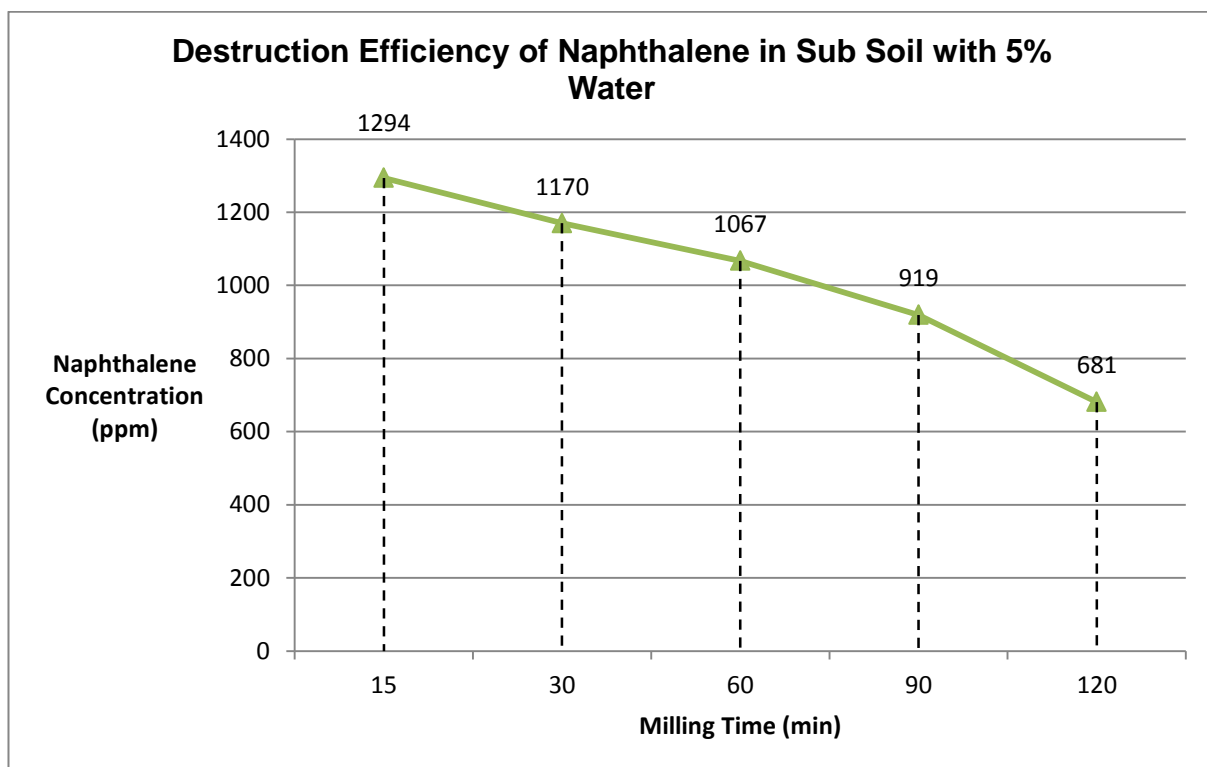
Destruction Efficiency of Naphthalene in Sub Soil with 10% Water
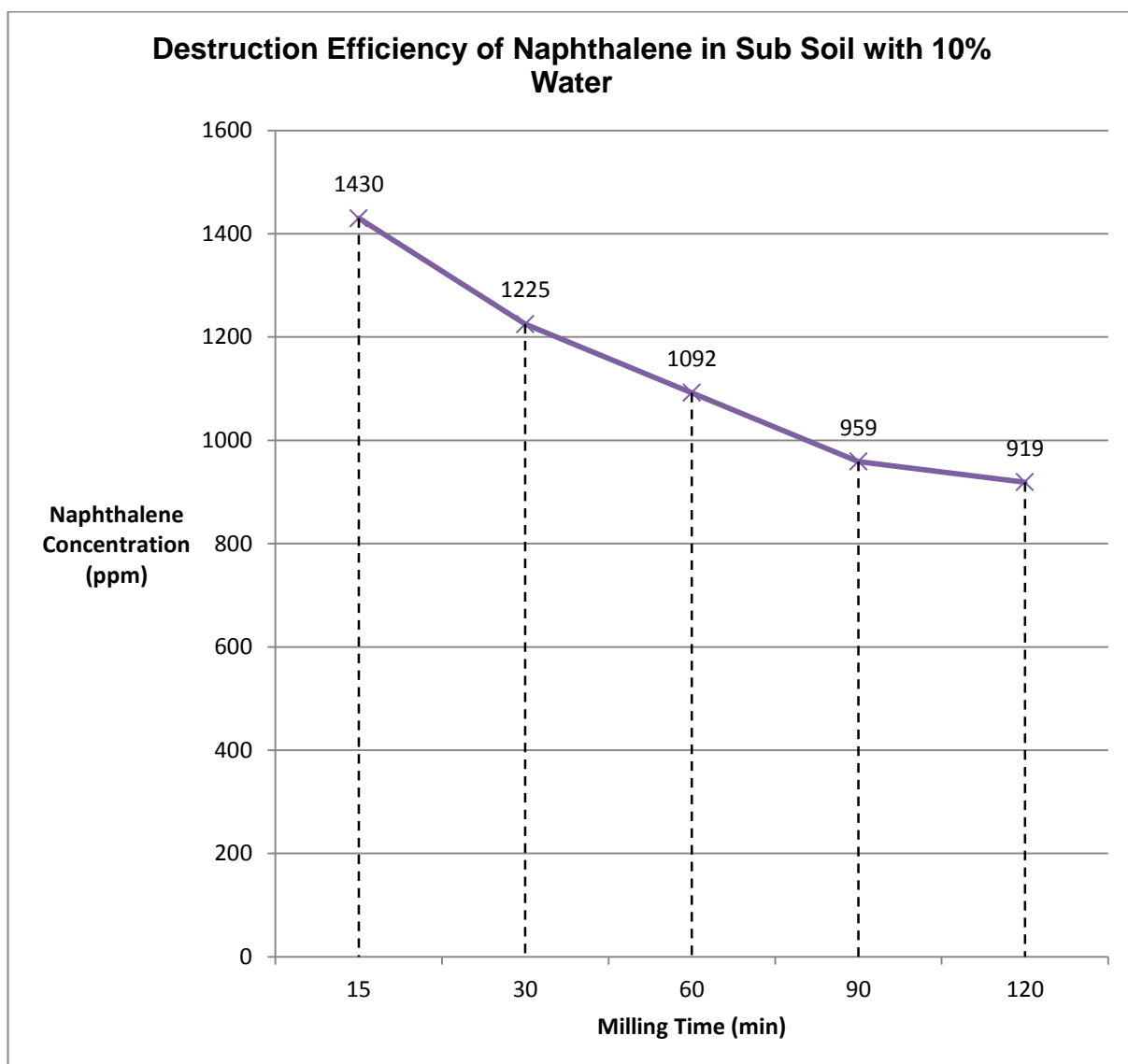
6.3.4.5 Discussion of Sub Soil Moisture Trials

Milling Interval (min)	No Added Water Naphthalene Conc. (ppm)	No Added Water Destruction Rate (%)
0	5000	0
15	1225	76
30	1057	79
60	921	82
90	742	85
120	651	87
Milling Interval (min)	**2% Water Naphthalene Conc. (ppm)**	**2% Water Destruction Rate (%)**
0	5000	0
15	1245	75
30	1162	77
60	1058	79
90	846	83
120	680	86
Milling Interval (min)	**5% Water Naphthalene Conc. (ppm)**	**5% Water Destruction Rate (%)**
0	5000	0
15	1294	74
30	1170	77
60	1067	79
90	919	82
120	681	86
Milling Interval (min)	**10% Water Naphthalene Conc. (ppm)**	**10% Water Destruction Rate (%)**
0	5000	0
15	1430	71
30	1225	76
60	1092	78
90	959	81
120	919	82

Destruction Efficiency of Naphthalene in Sub Soil with Different Water Concentrations

Naphthalene Destruction Rates in Subsoil at Different Water Concentrations
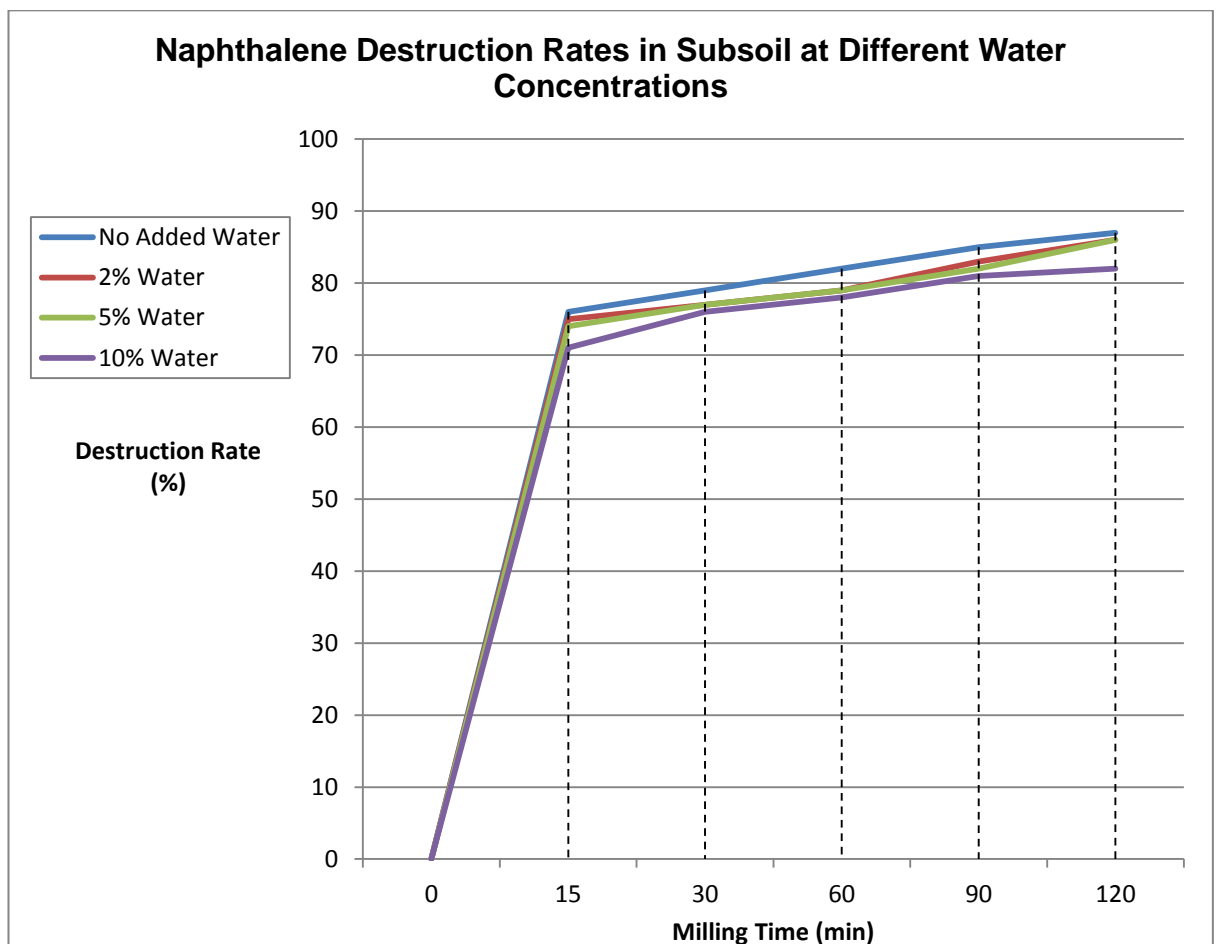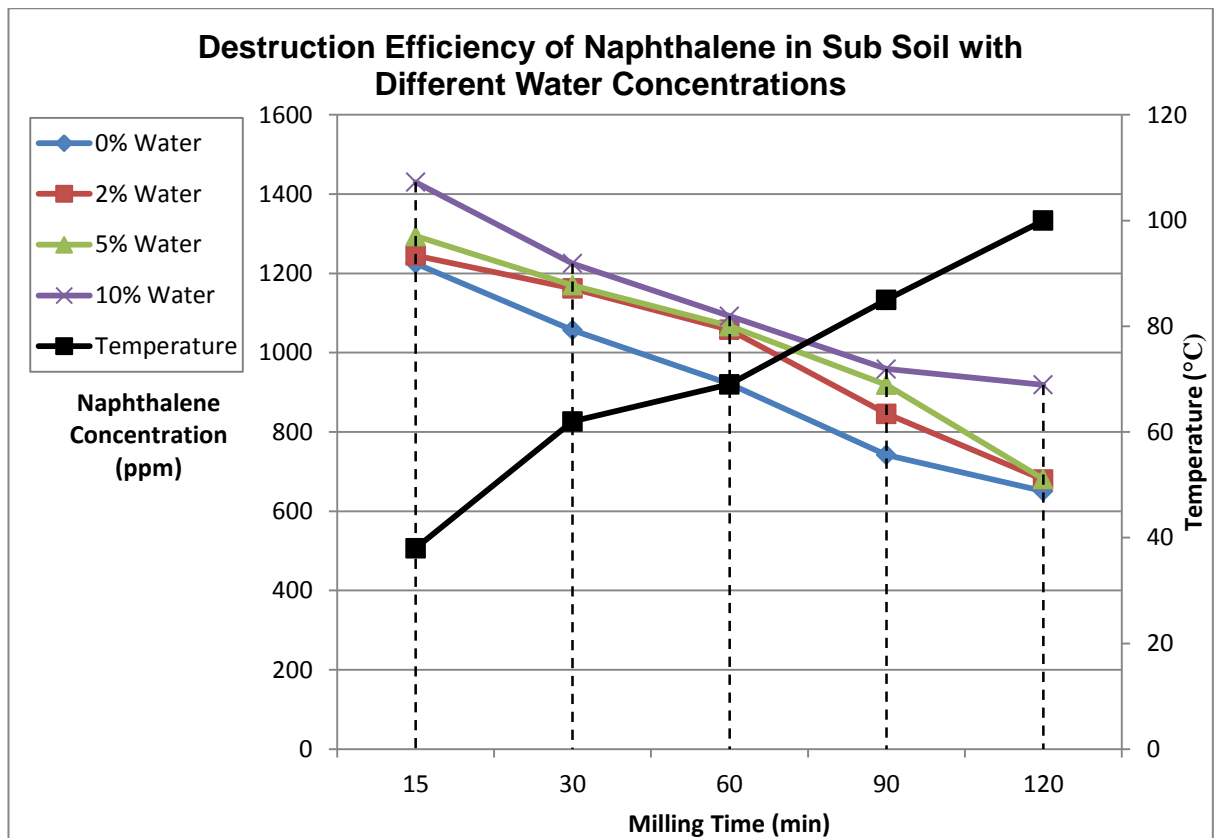
Mill Interval Destruction Rates vs Water concentration in Subsoil

Legend:
- 15min Naphthalene Conc   R² = 0.9143
- 30min Naphthalene Conc   R² = 0.8526
- 60min Naphthalene Conc   R² = 0.8
- 90min Naphthalene Conc   R² = 0.9657
- 120min Naphthalene Conc   R² = 0.7627

X-axis: Water Concentration (%) — No Added Water, 2% Water, 5% Water, 10% Water

Y-axis: Naphthalene Concentration (ppm)
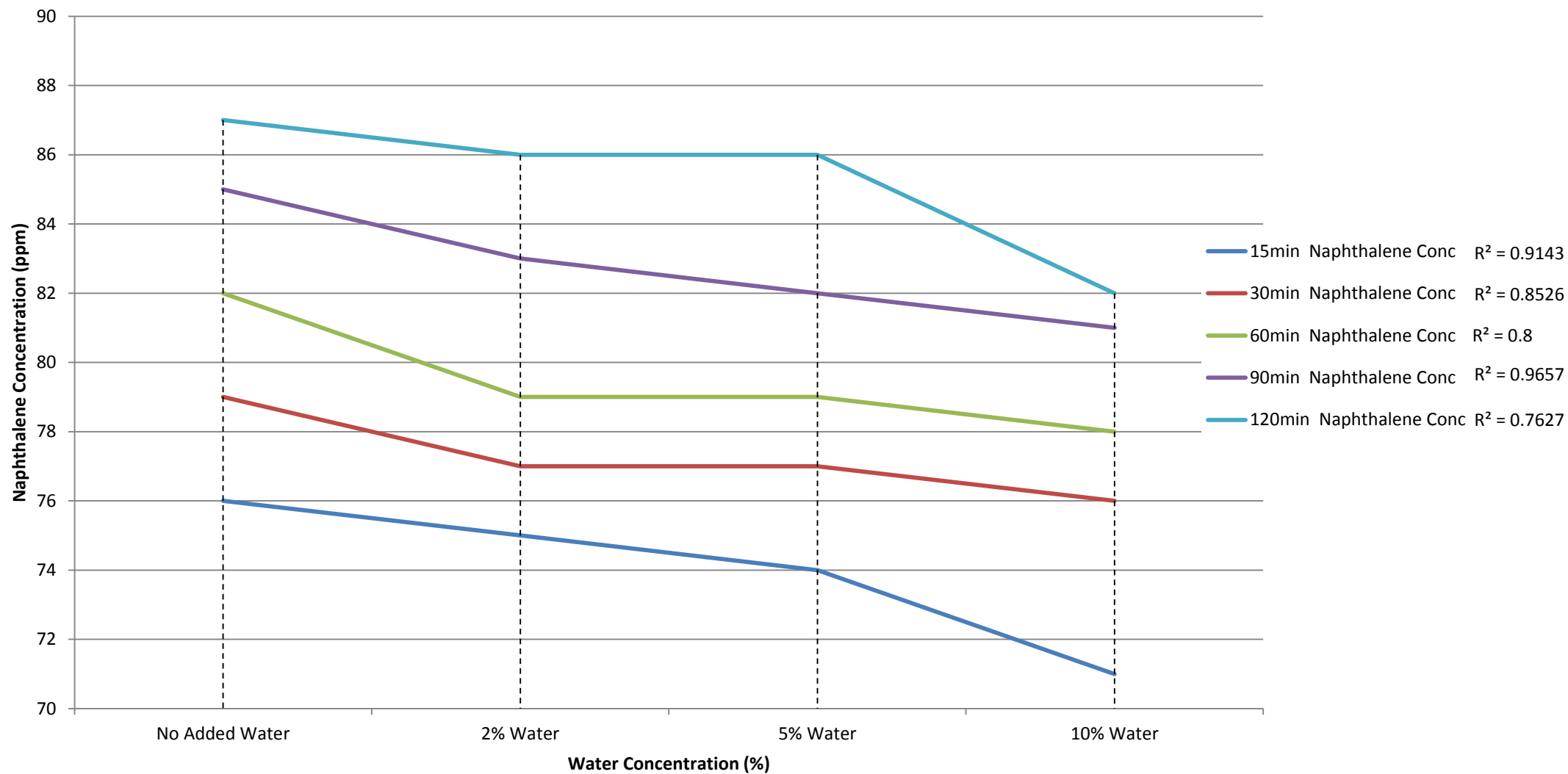
The subsoil moisture trial results once again followed the same pattern as the previous soils. The destruction rate of naphthalene decreased as water concentration increased. Destruction rates did experience a slight increase during the 120 minute milling interval as a result of the double effect of increased mechanical energy coupled with temperatures reaching water boiling point.

Water induced intermediates were only found in the 10% water concentration trial as follows:
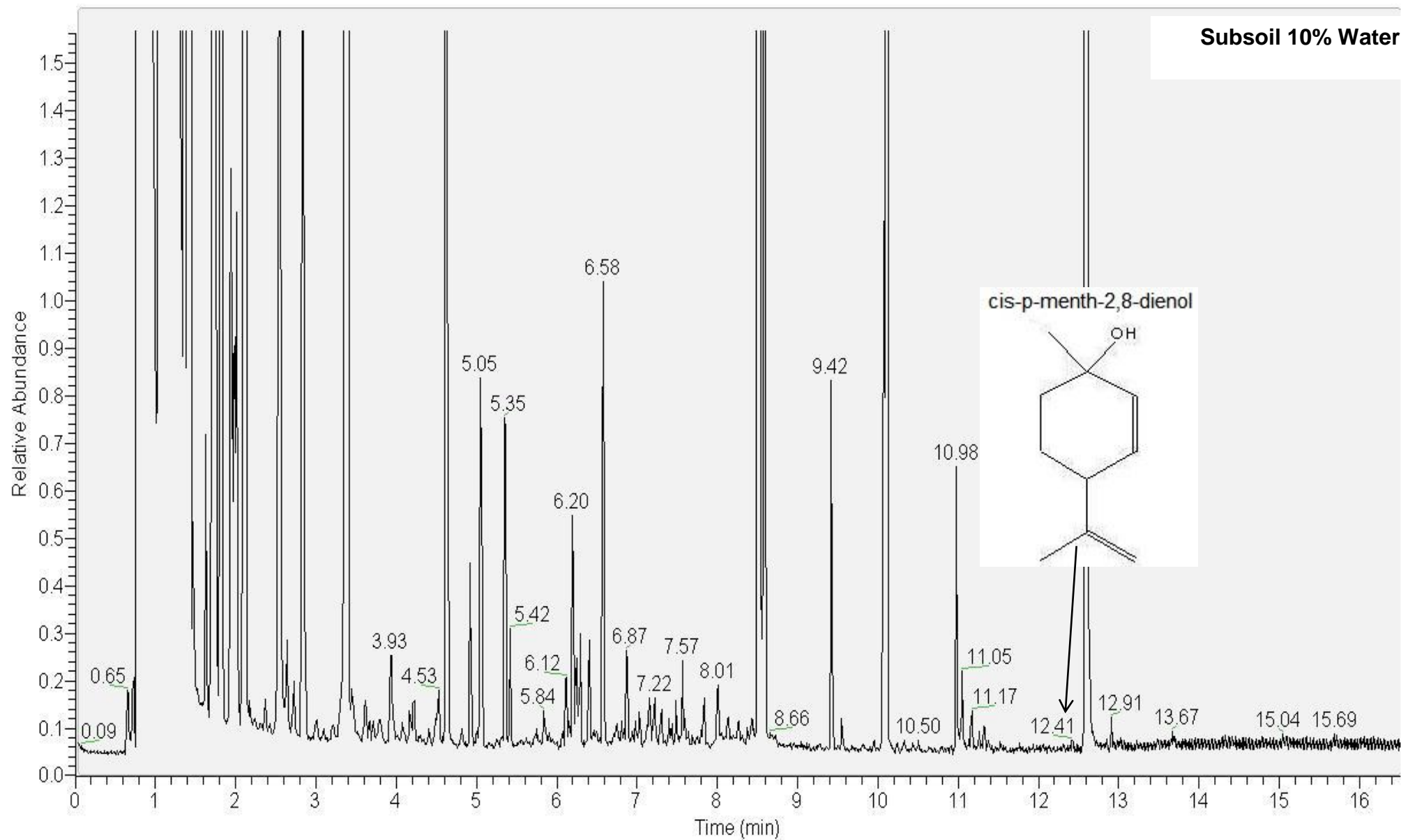
6.4 Organic Content Trials

A study in the effects of organic content on mechanochemical destruction of naphthalene was carried out. Cellulose powder was used as the organic model. Three soils, limestone, quartz and sub soil were used in the study. Four 50 grams samples of each soil were measured out and cellulose was added to each to make final cellulose contents of 0, 2, 5 and 10%. Each sample was milled at intervals of 15, 30, 60, 90 and 120 minutes.

6.4.1 Limestone Organic Content Trials

Four 50g samples of limestone with 0, 2, 5 and 10% cellulose content were milled to study the effect of organic content on the MCD process.

6.4.1.1 Limestone 0% Cellulose
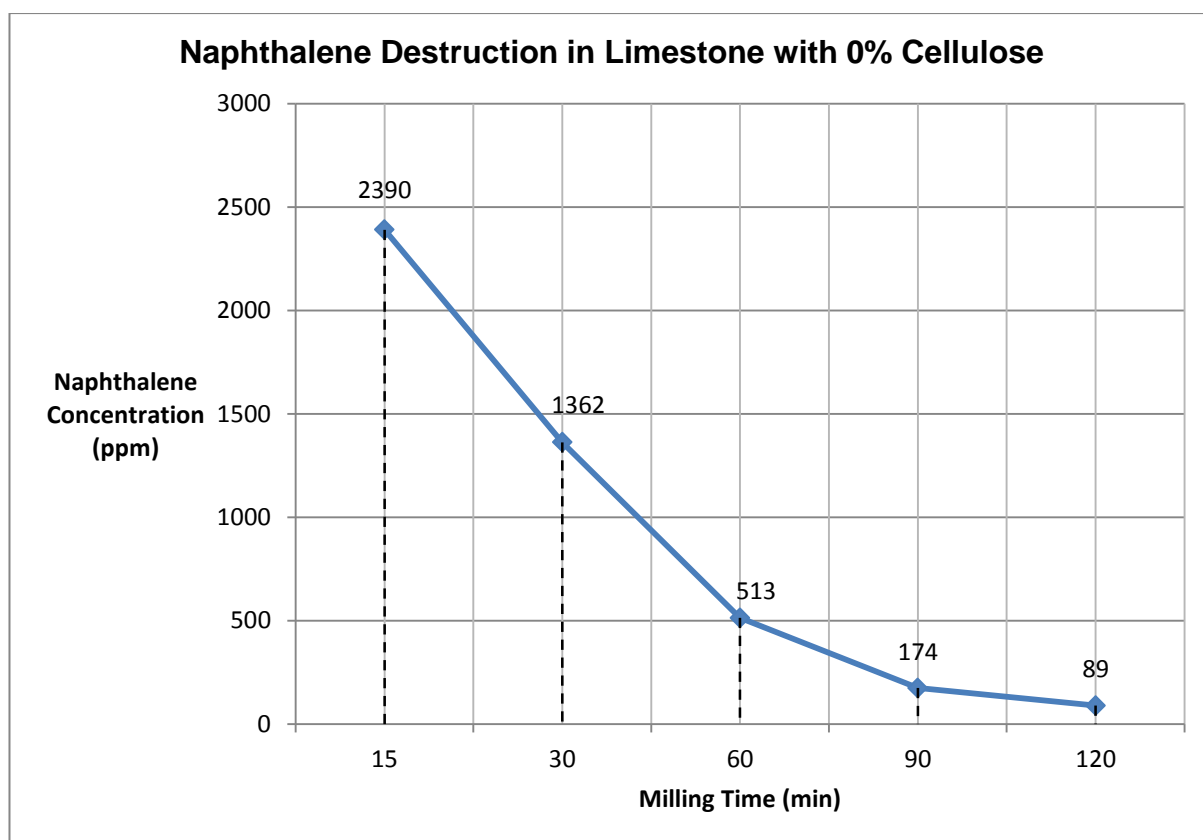
6.4.1.2 Limestone 2% Cellulose

Naphthalene Destruction in Limestone with 2% Cellulose
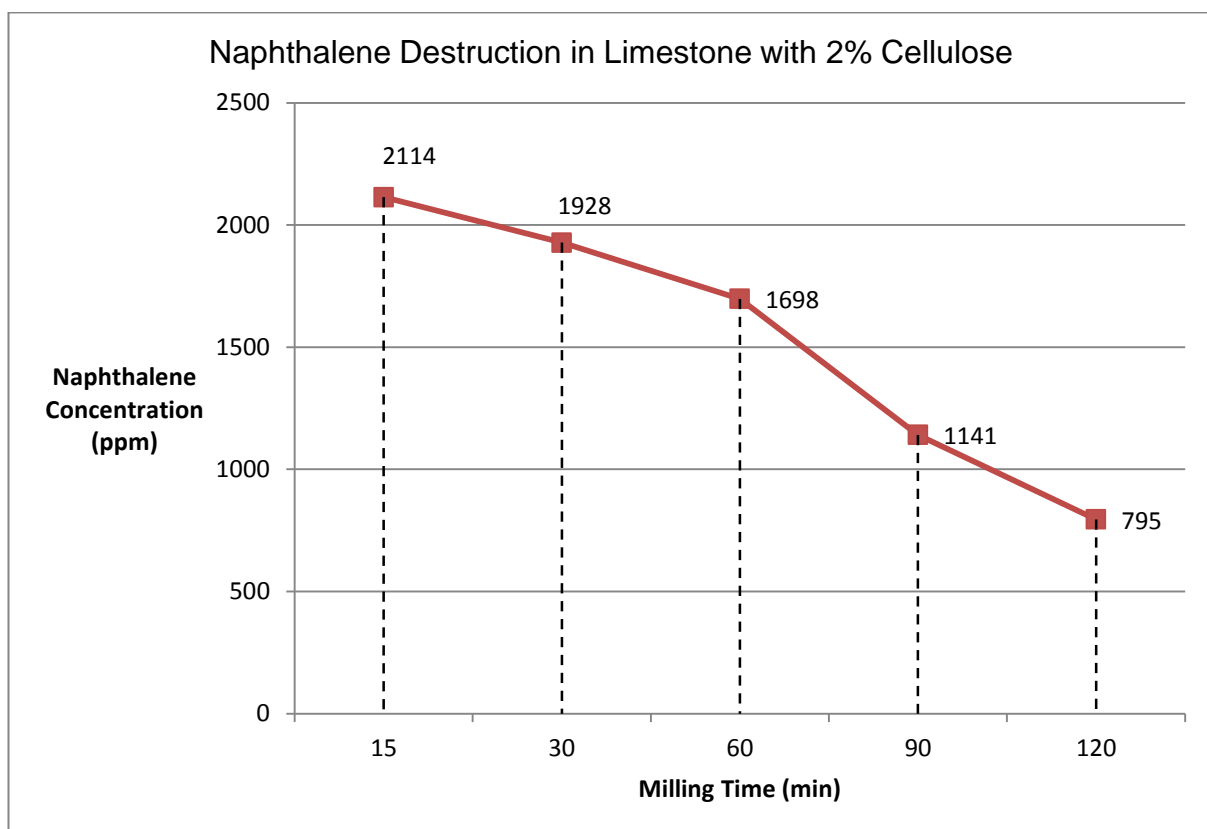
6.4.1.3 Limestone 5% Cellulose

Naphthalene Destruction in Limestone with 5% Cellulose
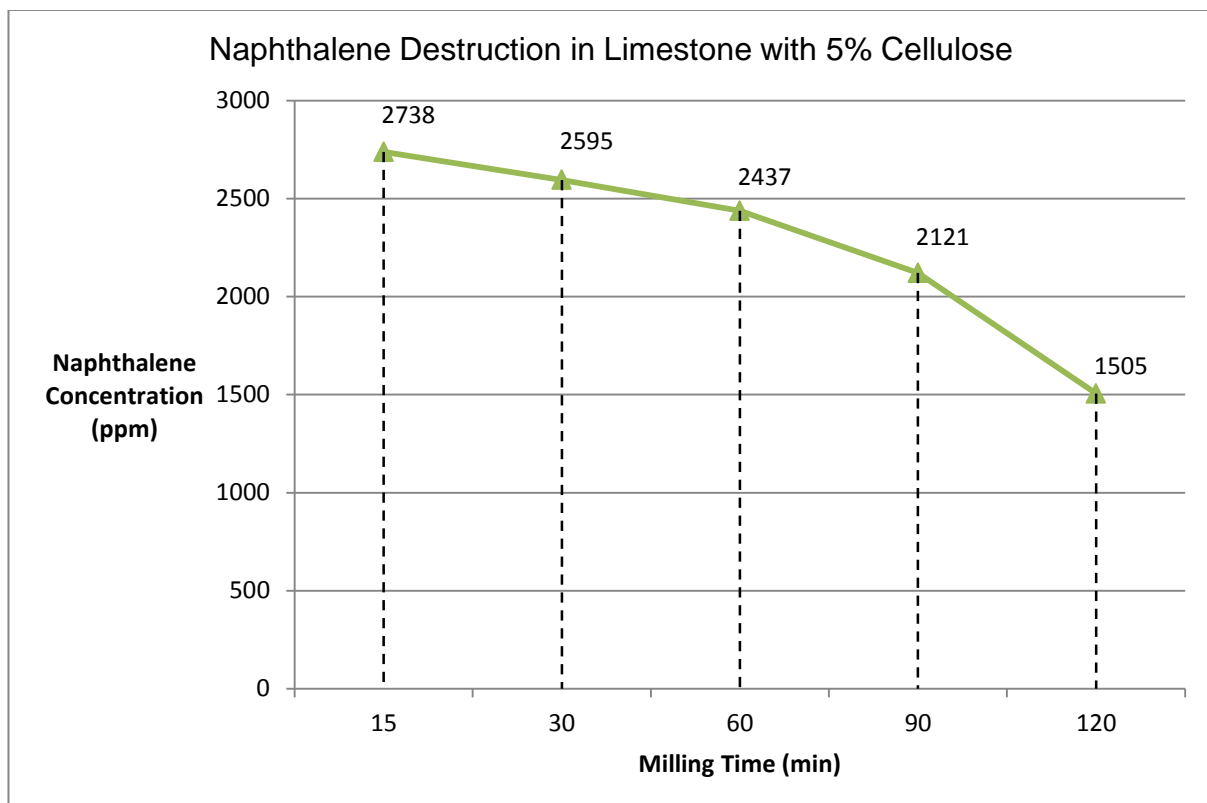
6.4.1.4 Limestone 10% Cellulose

Naphthalene Destruction in Limestone with 10% Cellulose
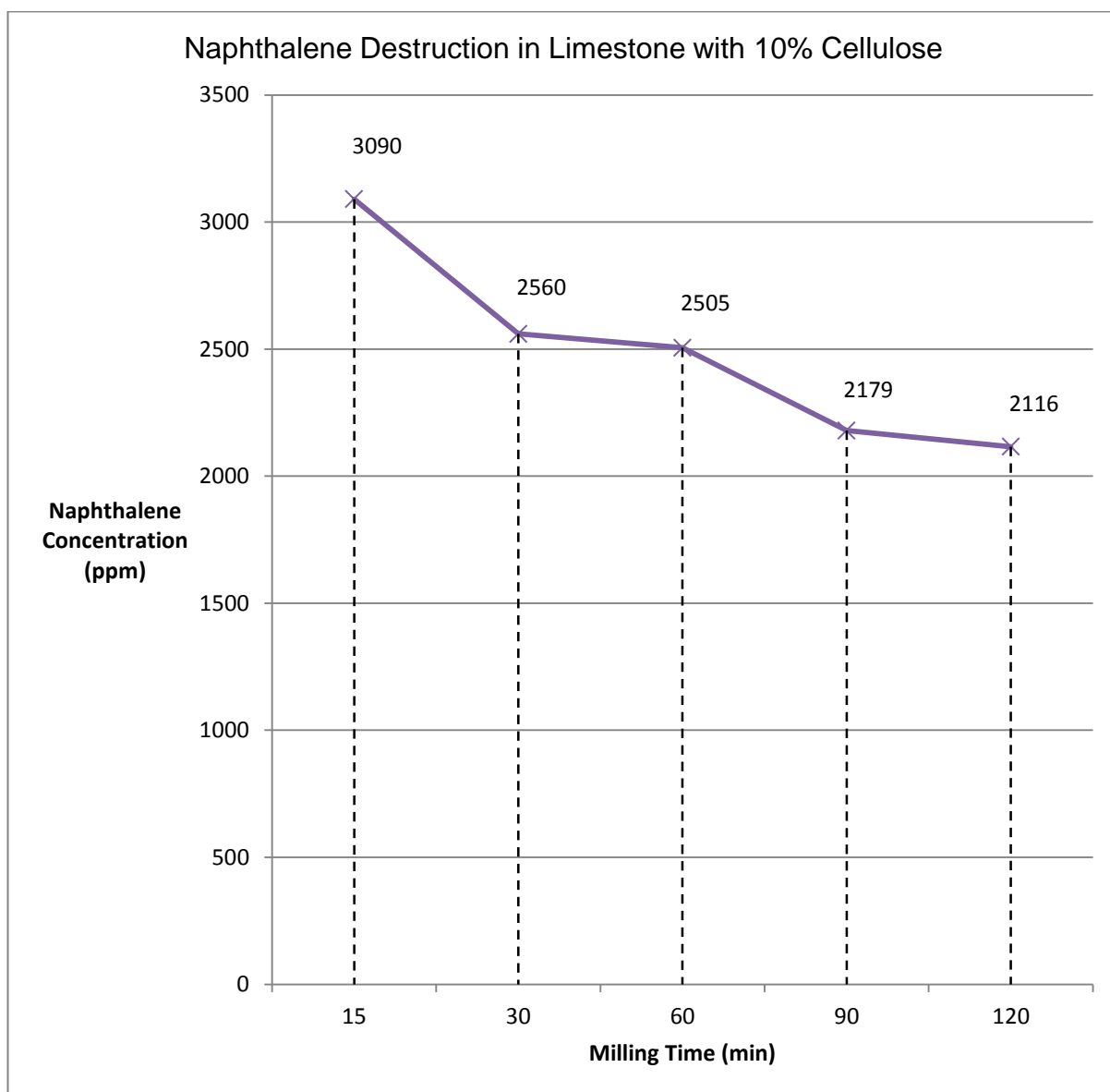
6.4.1.5 Discussion of Limestone Cellulose Content

Milling Interval (min)	No Added Cellulose Naphthalene Conc. (ppm)	No Added Cellulose Destruction Rate (%)
0	5000	0
15	2390	52
30	1362	73
60	513	90
90	174	97
120	89	98
Milling Interval (min)	2% Cellulose Naphthalene Conc. (ppm)	2% Cellulose Destruction Rate (%)
0	5000	0
15	2114	58
30	1928	61
60	1698	66
90	1141	77
120	795	84
Milling Interval (min)	5% Cellulose Naphthalene Conc. (ppm)	5% Cellulose Destruction Rate (%)
0	5000	0
15	2738	45
30	2595	48
60	2437	51
90	2121	58
120	1505	70
Milling Interval (min)	10% Cellulose Naphthalene Conc. (ppm)	10% Cellulose Destruction Rate (%)
0	5000	0
15	3090	38
30	2560	49
60	2505	50
90	2179	56
120	2116	58

Effect of Organic Content on the Destruction efficiency
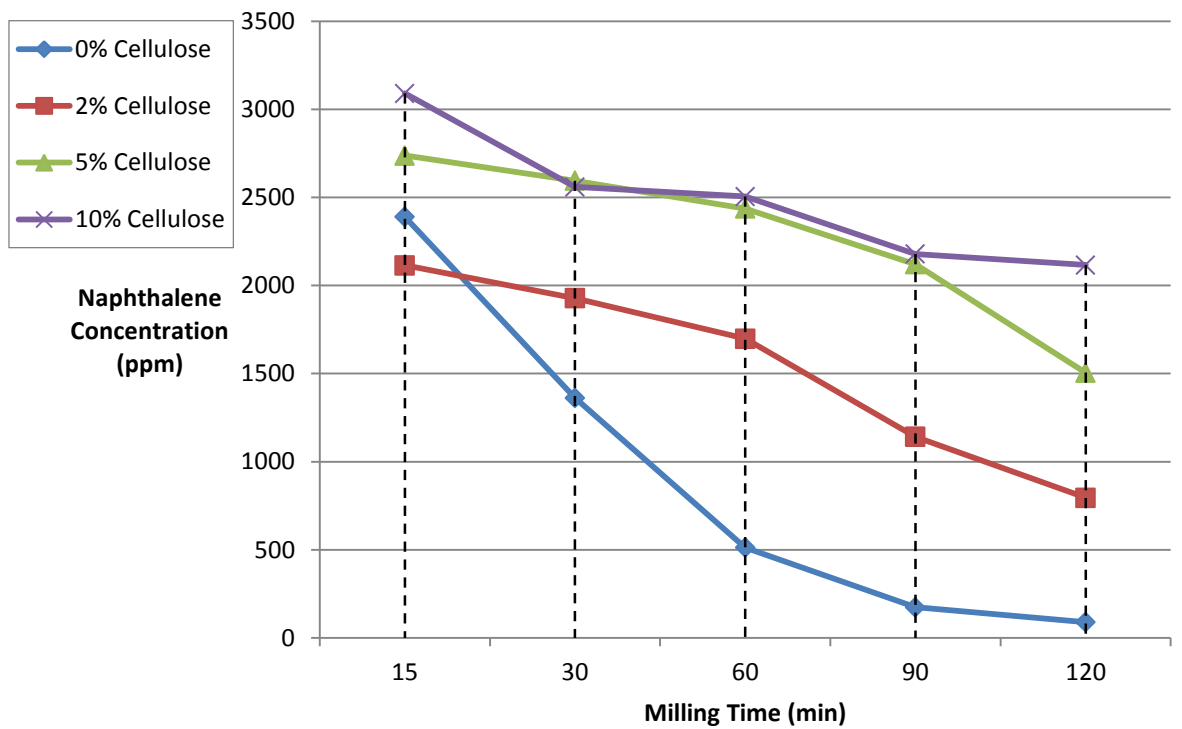
Destruction Rate of Naphthalene in Limestone with Different Concentrations of Cellulose
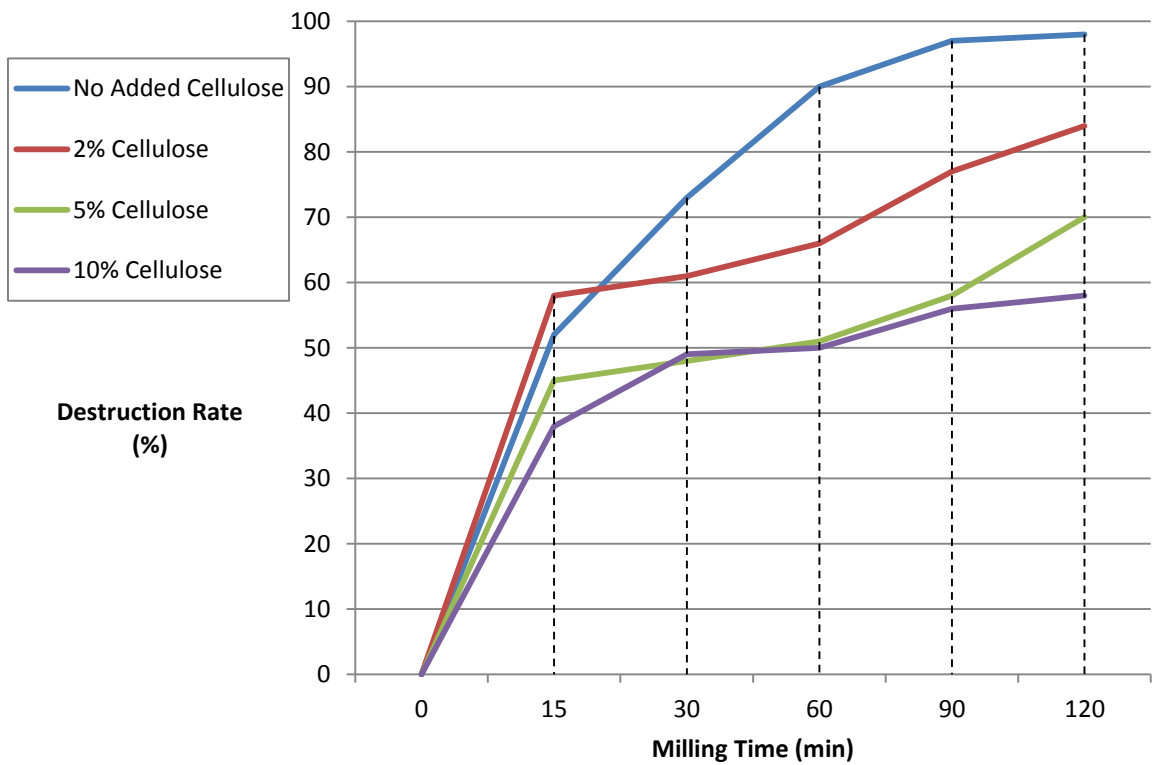
Cellulose has a detrimental effect on the destruction rates of naphthalene in limestone. As cellulose concentration increases, the naphthalene destruction rate decreases. The cause of this was thought to be radical scavenging by the cellulose. This scavenging will decrease the total amount of free radicals therefore, decreasing the amount that would have degraded the naphthalene molecules.

## 6.4.2 Quartz Organic Content Trials

Four 50g samples of quartz with 0, 2, 5 and 10% cellulose content were milled to study the effect of organic content on the MCD process.

6.4.2.1 Quartz 0% Cellulose

6.4.2.2 Quartz 2% Cellulose

Naphthalene Destruction in Quartz with 2% Cellulose

Naphthalene Concentration (ppm) vs Milling Time (min)

- 15 min: 1500
- 30 min: 2147
- 60 min: 912
- 90 min: 40
- 120 min: 10

6.4.2.3 Quartz 5% Cellulose

Naphthalene Destruction in Quartz with 5% Cellulose

Naphthalene Concentration (ppm) vs Milling Time (min)

- 15 min: 433
- 30 min: 1398
- 60 min: 844
- 90 min: 503
- 120 min: 135
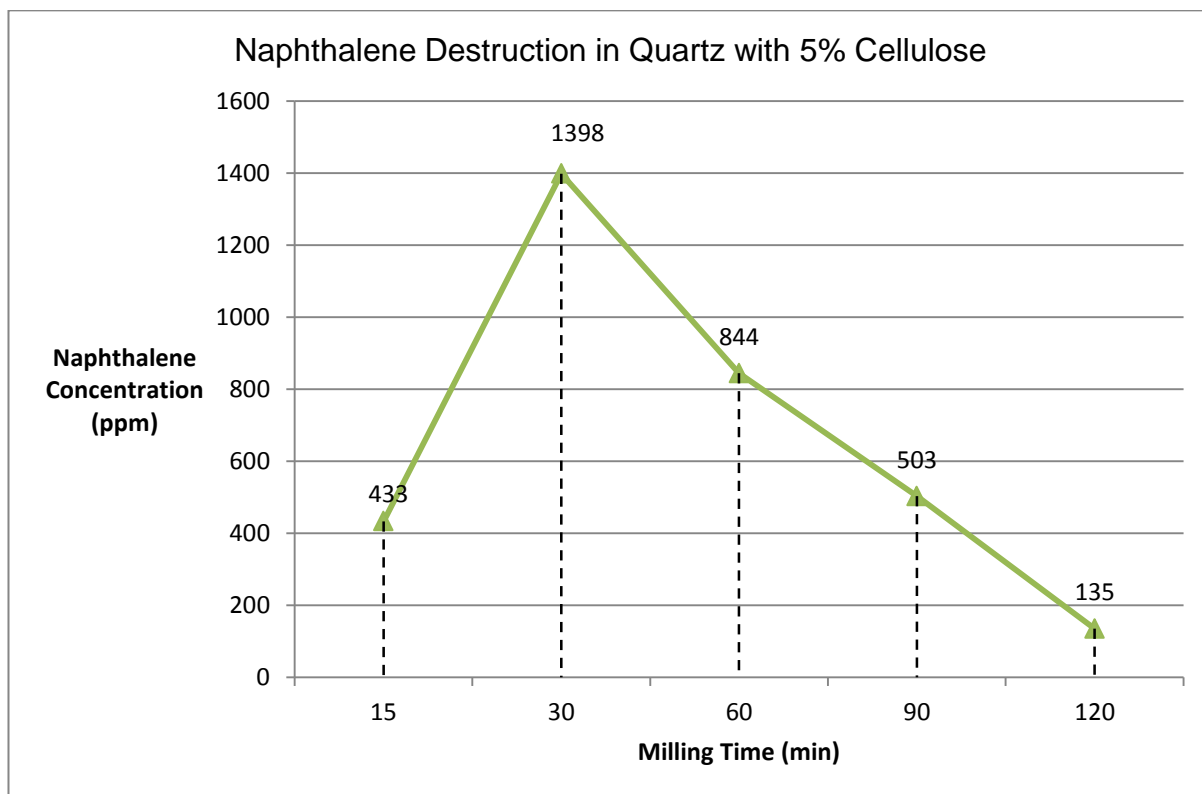
## 6.4.2.4 Quartz 10% Cellulose


Naphthalene Destruction in Quartz with 10% Cellulose
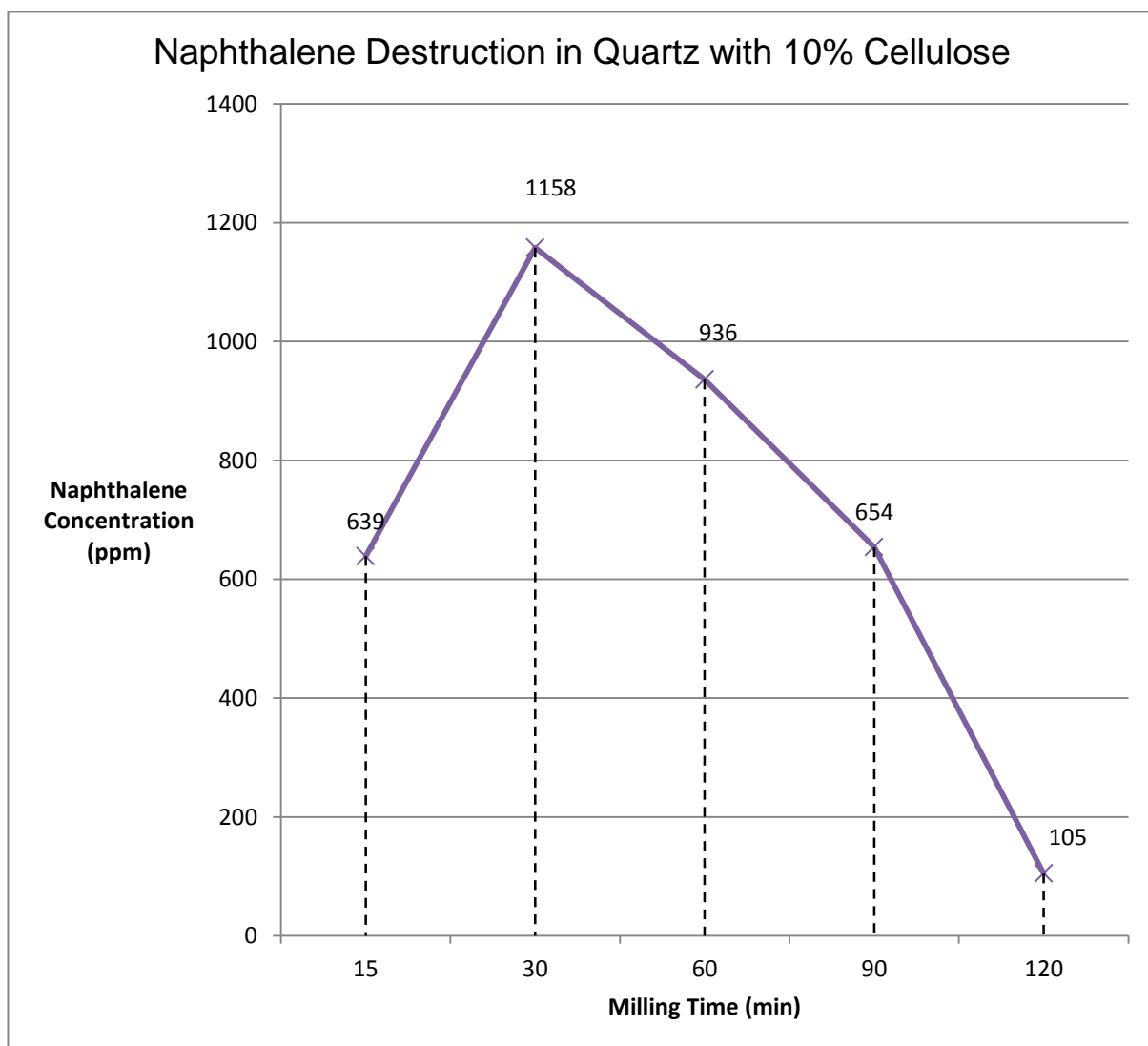
6.4.2.5 Discussion of Quartz Cellulose Content

Milling Interval (min)	No Added Cellulose Naphthalene Conc. (ppm)	No Added Cellulose Destruction Rate (%)
0	5000	0
15	442	91
30	10	100
60	2	100
90	2	100
120	1	100
Milling Interval (min)	2% Cellulose Naphthalene Conc. (ppm)	2% Cellulose Destruction Rate (%)
0	5000	0
15	1500	70
30	2147	57
60	912	82
90	40	99
120	10	100
Milling Interval (min)	5% Cellulose Naphthalene Conc. (ppm)	5% Cellulose Destruction Rate (%)
0	5000	0
15	433	91
30	1398	72
60	844	83
90	503	90
120	135	97
Milling Interval (min)	10% Cellulose Naphthalene Conc. (ppm)	10% Cellulose Destruction Rate (%)
0	5000	0
15	639	87
30	1158	77
60	936	81
90	654	87
120	105	98

Effect of Organic Content on the Destruction efficiency

Destruction Rate of Naphthalene in Quartz with Different Concentrations of Cellulose

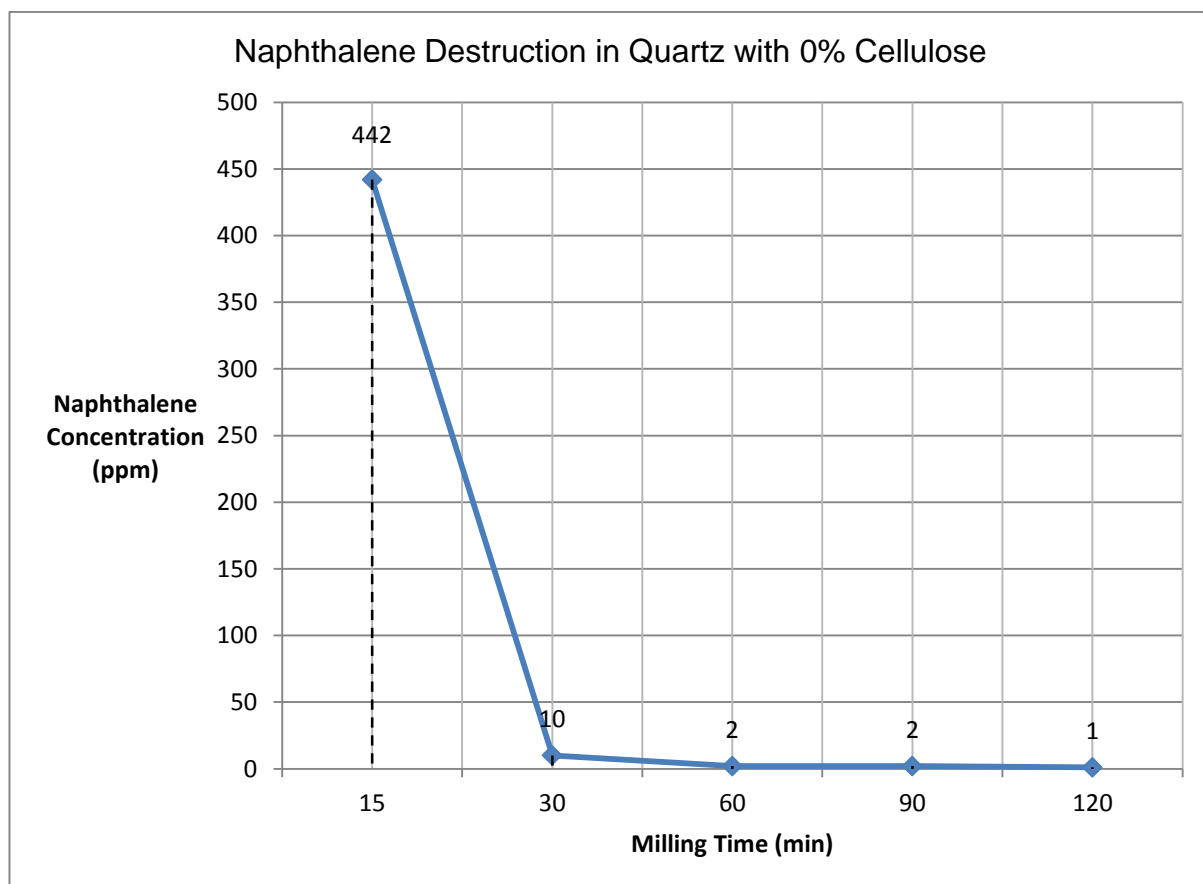164
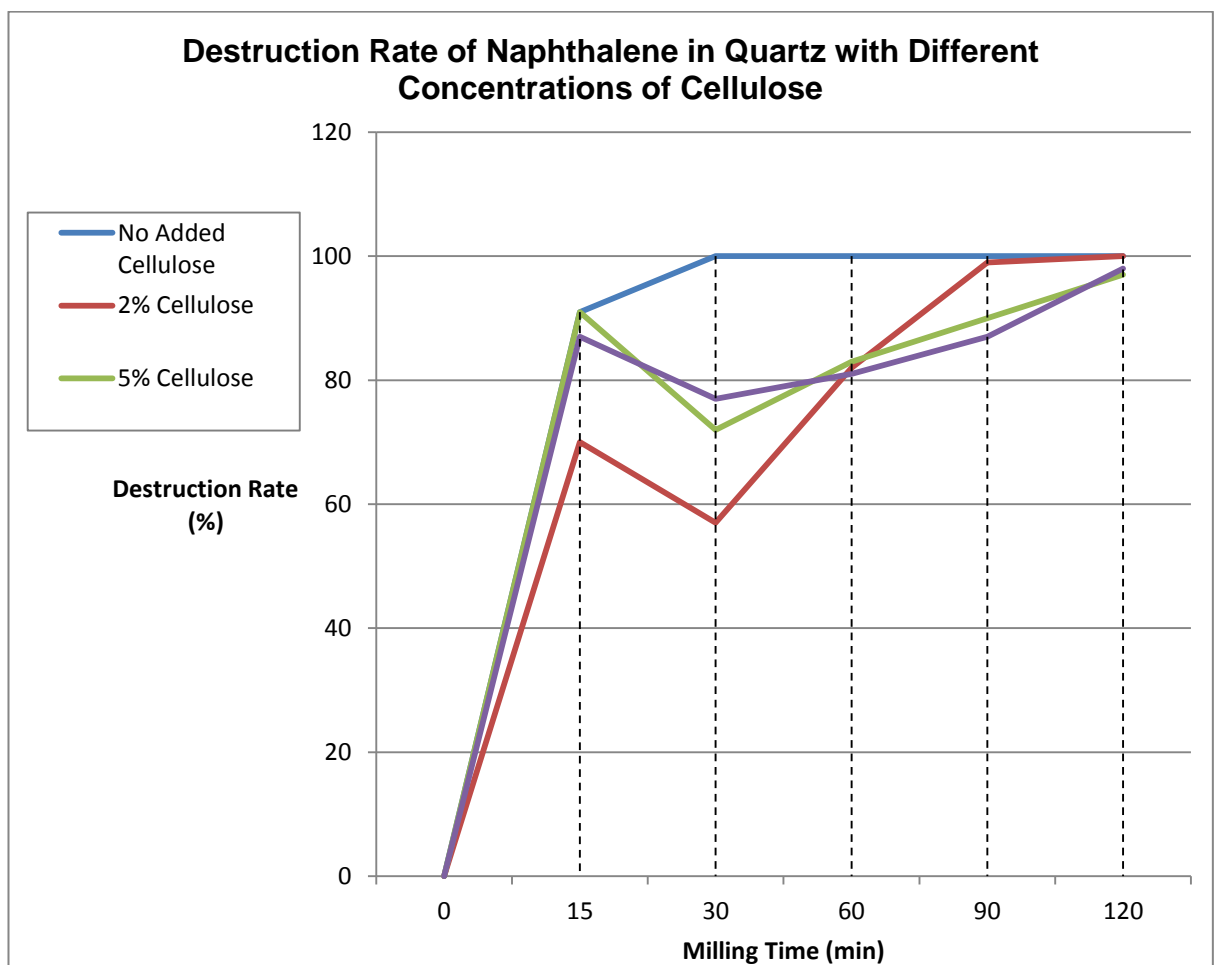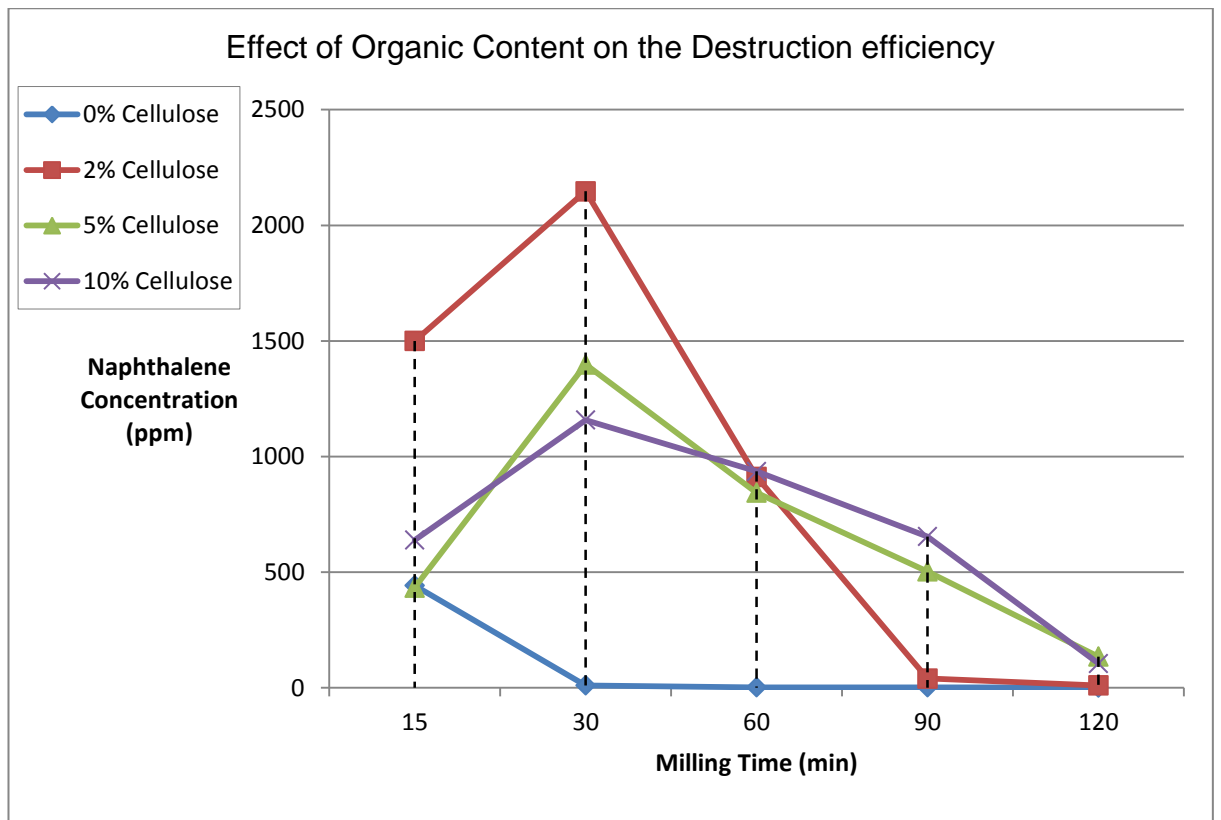
Cellulose also had a detrimental effect on the destruction rates of naphthalene in quartz. As cellulose concentration increases, the naphthalene destruction rate decreases. The cause of this was thought to be radical scavenging by the cellulose. This scavenging will decrease the total amount of free radicals therefore, decreasing the amount that would have degraded the naphthalene molecules.
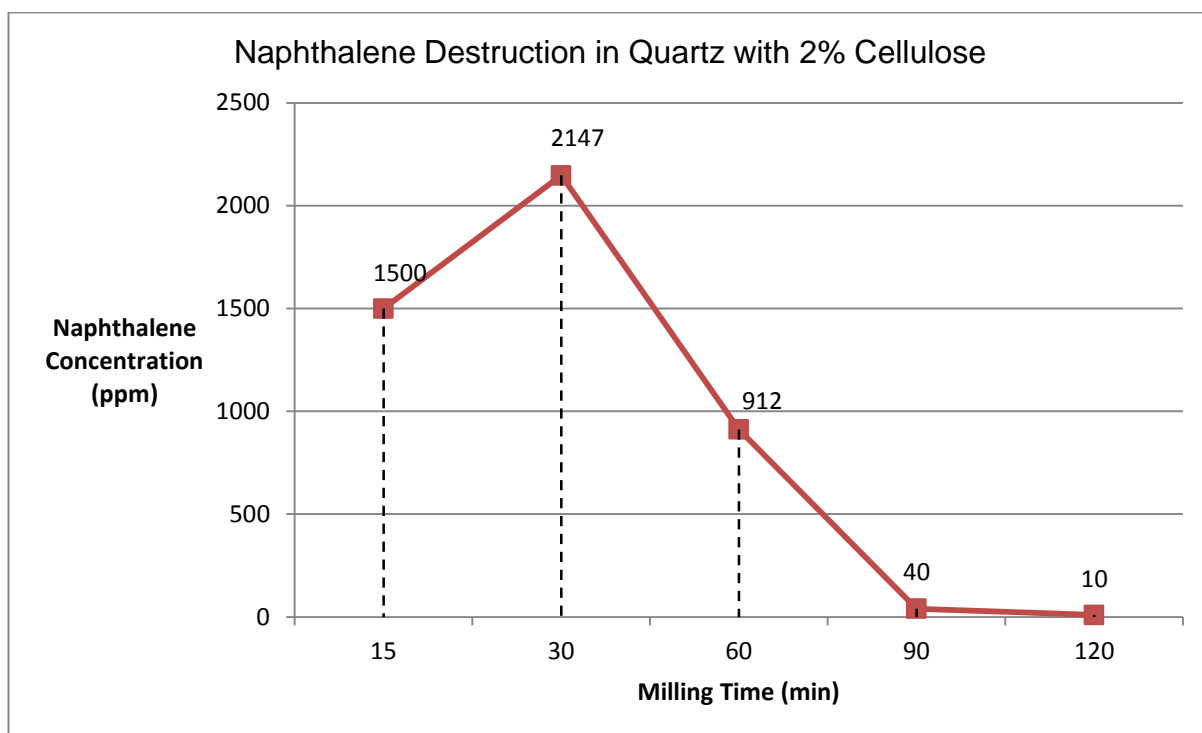
The difference between the effect cellulose had on limestone and quartz is that during the 30 minute quartz milling interval, there was a sharp increase of naphthalene concentration i.e. there was more naphthalene at the end of the 30 minute milling interval than at the 15 minute milling interval. At first glance this is counterintuitive, however the actions of activated cellulose suggests otherwise. A few studies into the sorptive capacity of cellulose in an environmental remediation context have determined that cellulose is able to sequester organic and inorganic pollutants very efficiently. Wu et. al published a paper on the removal of trichloroethylene from water by cellulose acetate in 2006. They concluded that the sorption of trichloroethylene by cellulose was very fast and reached equilibrium within 15 minutes (Wu 2006). Another paper published in 2002 by Shukla et. al on the role of sawdust in the removal of unwanted materials from water concluded that sawdust was proven to be a promising material for the removal of contaminants from waste waters. Not only is sawdust abundant, but also it is an efficient and economic adsorbent that is effective to many types of pollutants, such as, dyes, oil, salts and heavy metals (Shukla 2002). Therefore, the decrease of naphthalene concentration during the first milling interval is due to mechanochemical destruction and due to it being sequestered within the cellulose matrix.

From the 60 minute milling interval onwards, the naphthalene concentrations began to fall again i.e. the destruction rates increase. This is due to the complete degradation of cellulose. Once cellulose is degraded to such an extent, it no longer has the capacity to adsorb the naphthalene. The desorbed naphthalene is then continuingly degraded throughout the milling intervals and its concentrations decrease.

6.4.3 Sub Soil Organic Content Trials

Four 50g samples of sub soil with 0, 2, 5 and 10% cellulose content were milled to study the effect of organic content on the MCD process.

6.4.3.1 Sub Soil 0% Cellulose
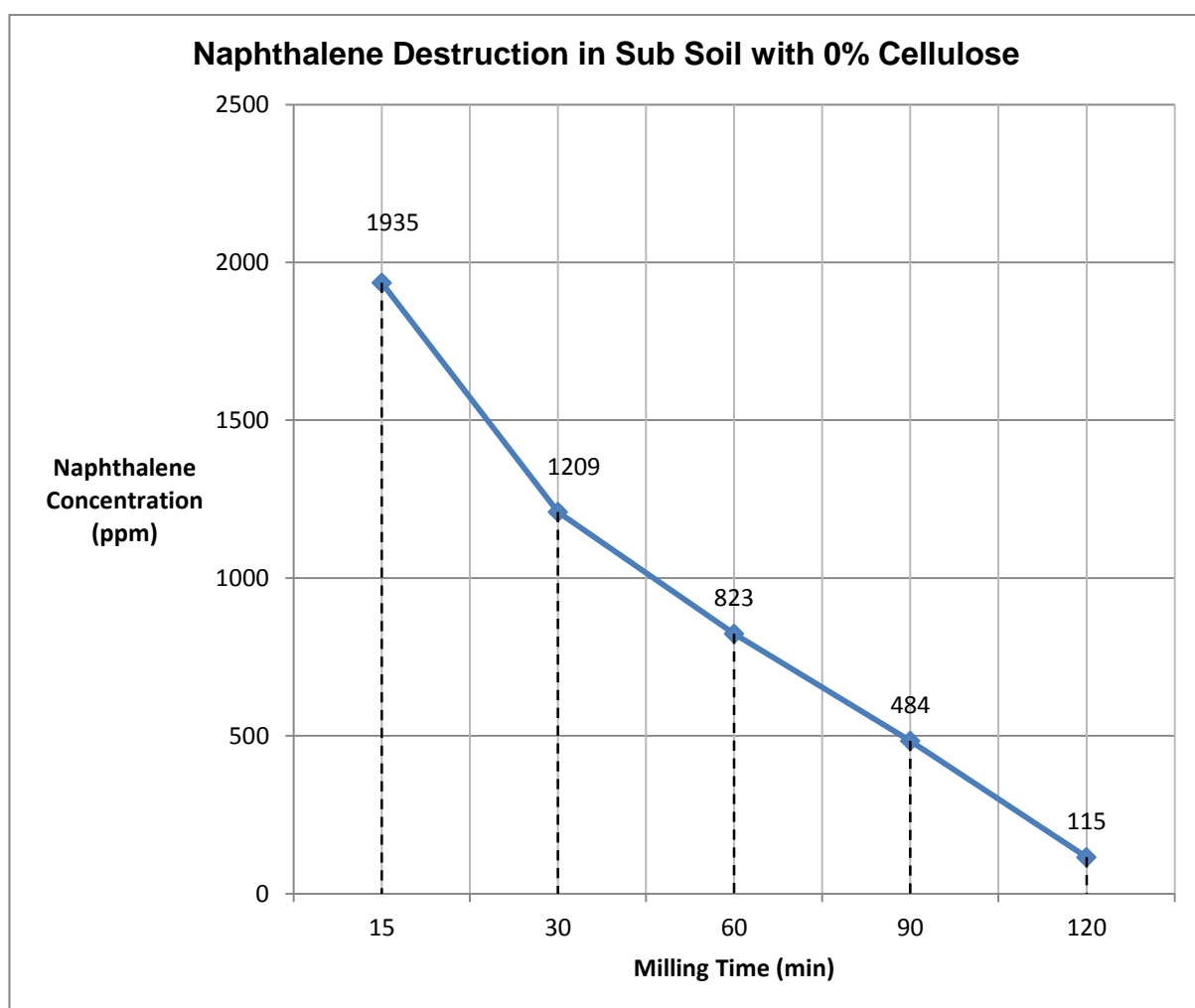
6.4.3.2 Sub Soil 2% Cellulose

Naphthalene Destruction in Sub Soil with 2% Cellulose
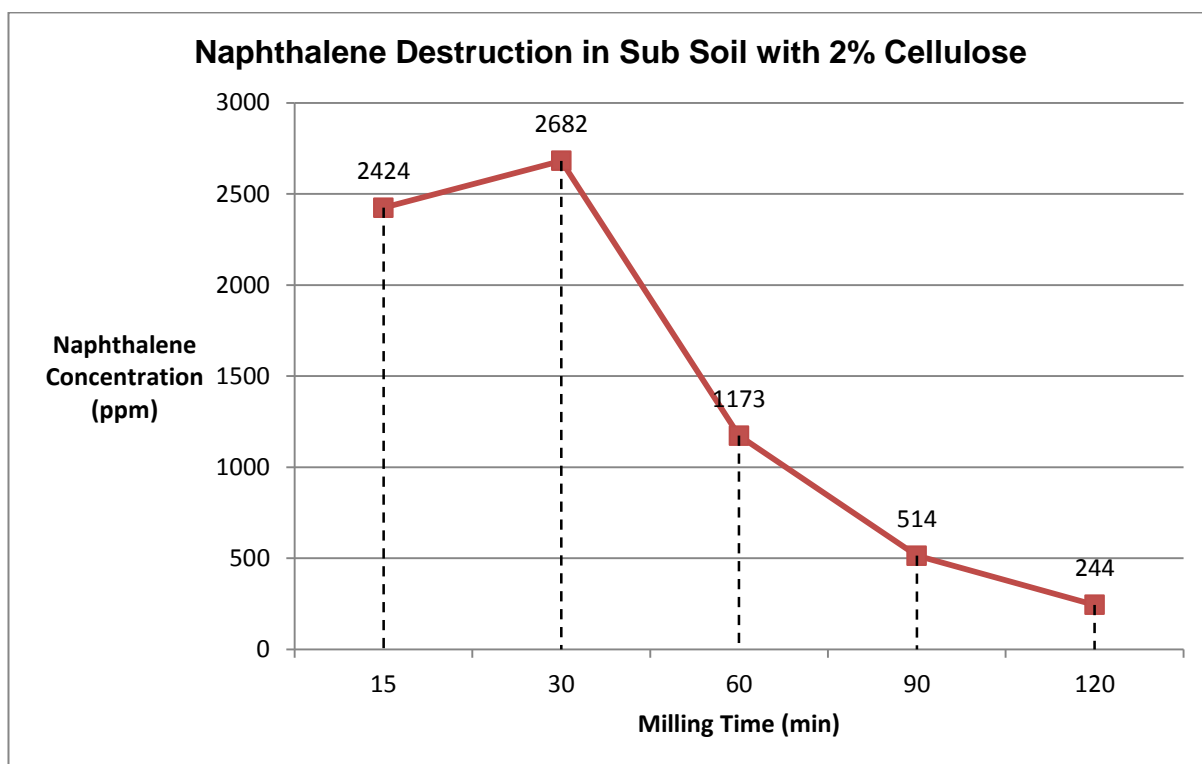
6.4.3.3 Sub Soil 5% Cellulose

Naphthalene Destruction in Sub Soil with 5% Cellulose
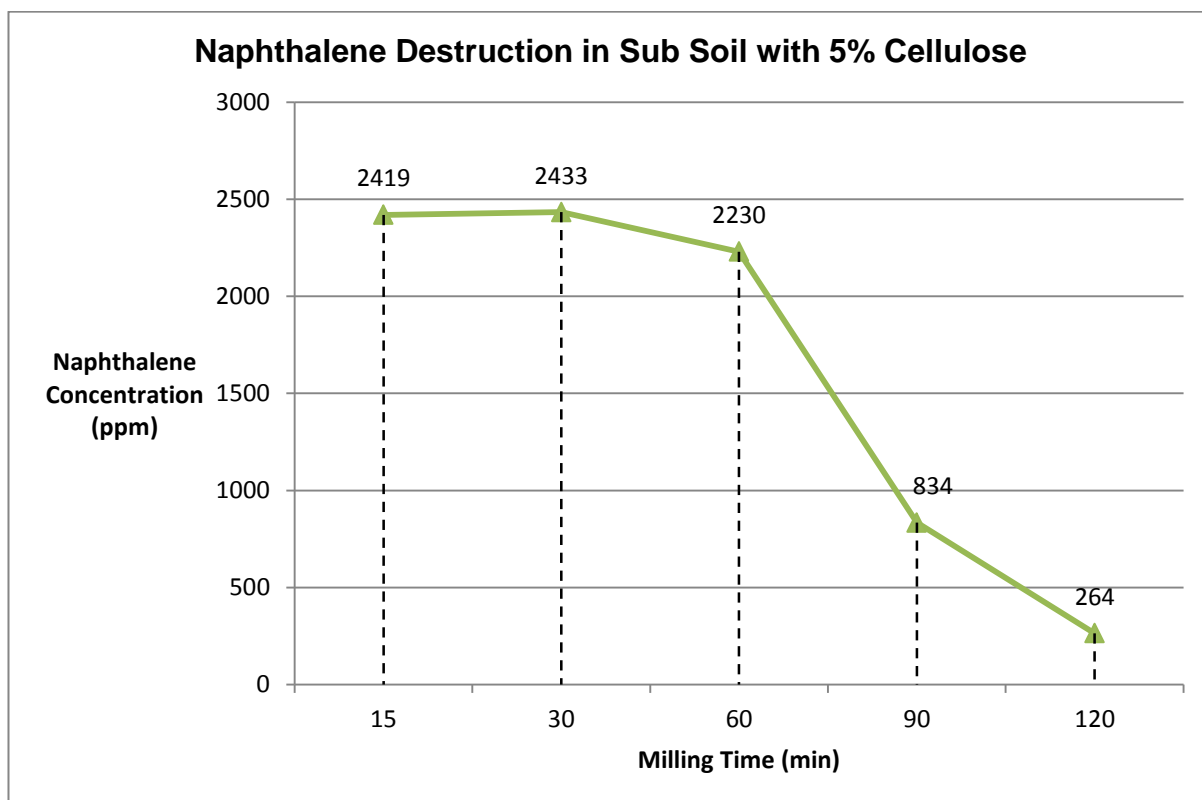
6.4.3.4 Sub Soil 10% Cellulose

Naphthalene Destruction in Sub Soil with 10% Cellulose
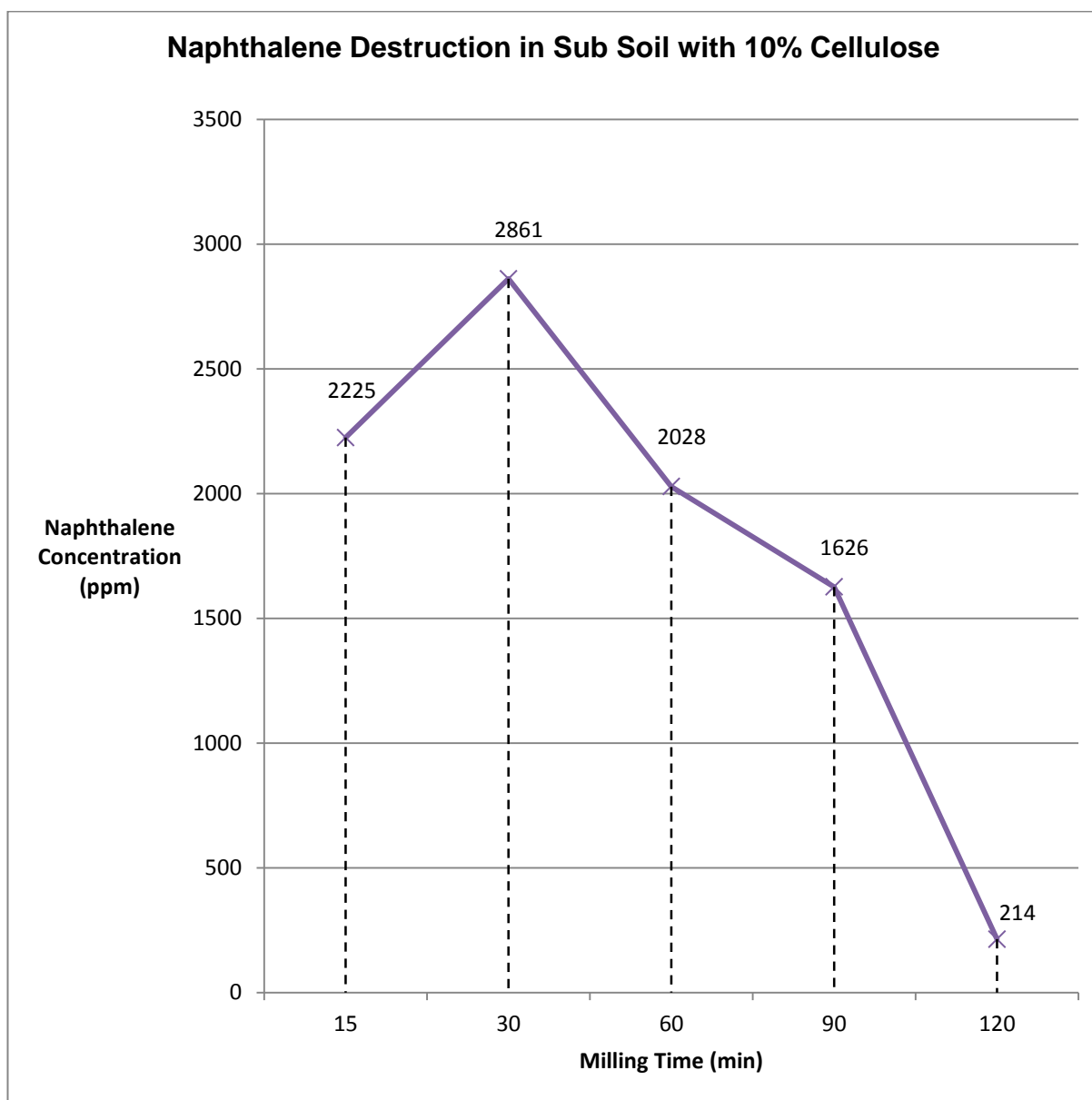
6.4.3.5 Discussion of Subsoil Cellulose Content

Milling Interval (min)	No Added Cellulose Naphthalene Conc. (ppm)	No Added Cellulose Destruction Rate (%)
0	5000	0
15	1935	61
30	1209	76
60	823	84
90	484	90
120	115	98
Milling Interval (min)	2% Cellulose Naphthalene Conc. (ppm)	2% Cellulose Destruction Rate (%)
0	5000	0
15	2424	52
30	2682	46
60	1173	77
90	514	90
120	244	95
Milling Interval (min)	5% Cellulose Naphthalene Conc. (ppm)	5% Cellulose Destruction Rate (%)
0	5000	0
15	2419	52
30	2433	51
60	2230	55
90	834	83
120	264	95
Milling Interval (min)	10% Cellulose Naphthalene Conc. (ppm)	10% Cellulose Destruction Rate (%)
0	5000	0
15	2225	56
30	2861	43
60	2028	59
90	1626	67
120	214	96

Effect of Organic Content on the Destruction Efficiency

Legend:
- 0% Cellulose
- 2% Cellulose
- 5% Cellulose
- 10% Cellulose

Naphthalene Concentration (ppm) vs Milling Time (min)

Destruction Rate of Naphthalene in Subsoil with Different Concentrations of Cellulose

Legend:
- No Added Cellulose
- 2% Cellulose
- 5% Cellulose
- 10% Cellulose

Destruction Rate (%) vs Milling Time (min)
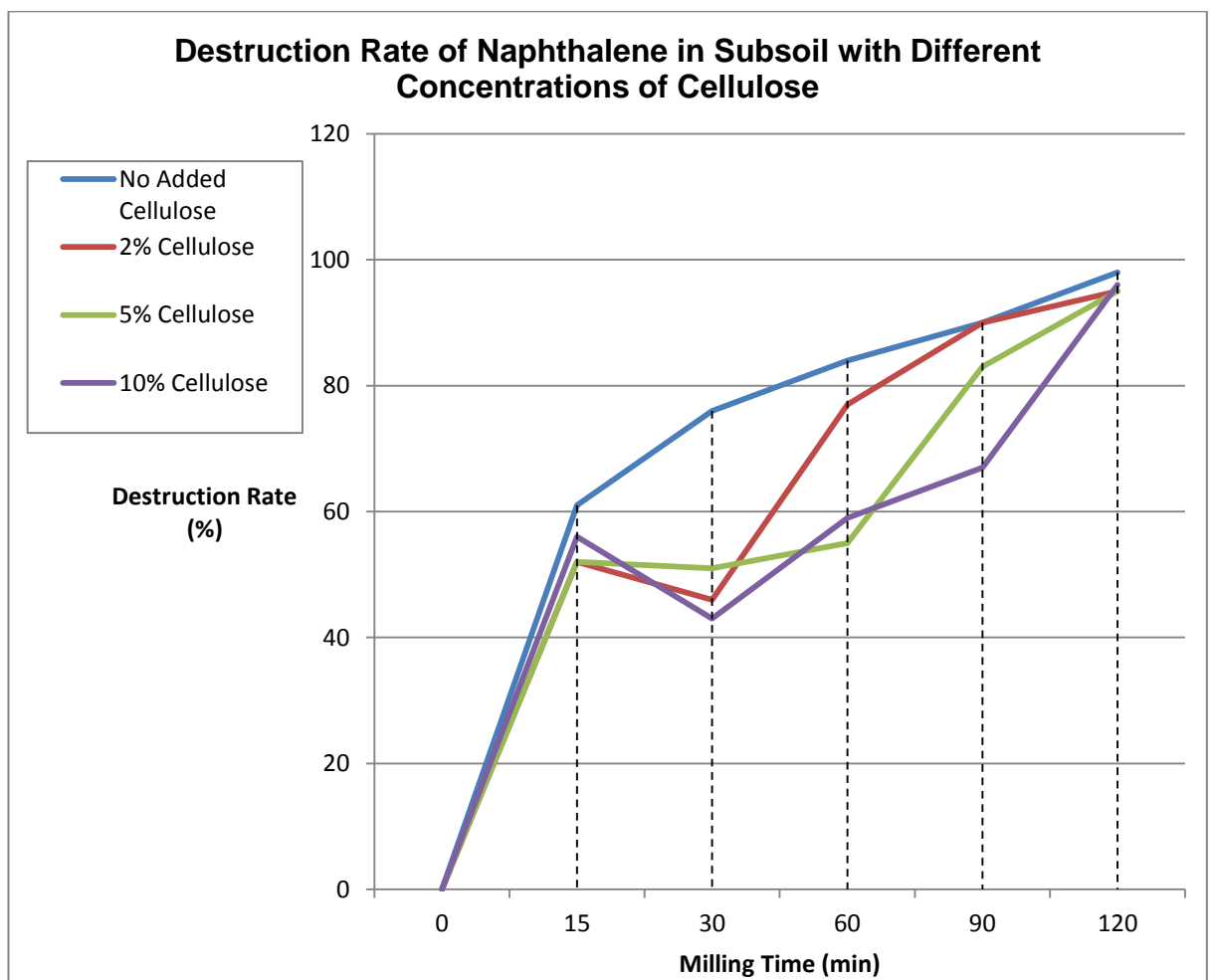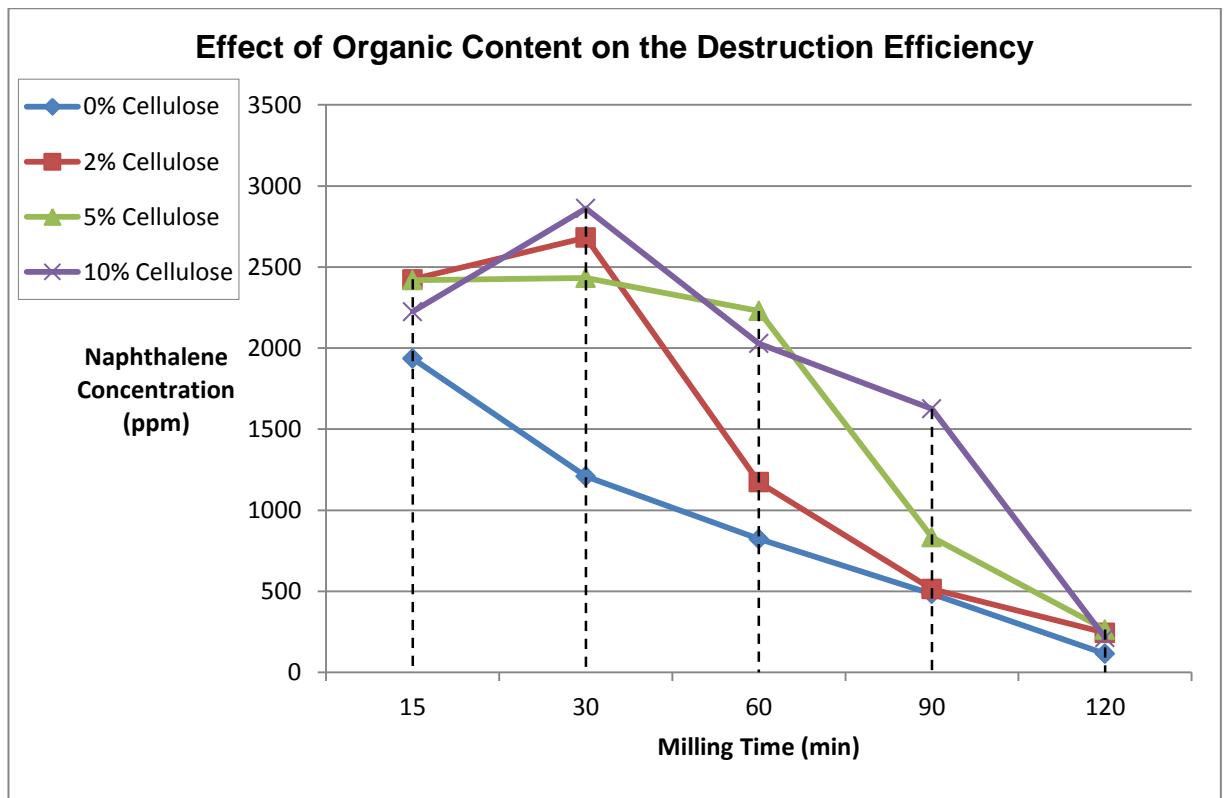
The cellulose in subsoil followed the same pattern of the quartz data. There was an initial reduction of naphthalene concentrations at the end of the 15 minute milling interval followed by a sharp increase at the 30 minute milling interval. From the 60 minute milling interval, there is a steady decrease of naphthalene concentration. Cellulose is also sequestering naphthalene when milled with subsoil but then is degraded during the 30 minute intervals which releases the formally adsorbed naphthalene. It is also evident that, overall, cellulose decreases the destruction rate of naphthalene.

6.5 Diesel Trials

A study on the mechanochemical destruction of diesel was carried out in four different soils. The four soils were limestone, quartz, scoria and subsoil. Four 50g samples of each soil were measured out and 10,000ppm diesel was added to each. Each sample was milled at intervals of 15, 30, 60, 90 and 120 minutes.

6.5.1 Limestone Diesel Trial

6.5.2 Quartz Diesel Trial

Diesel Destruction in Quartz
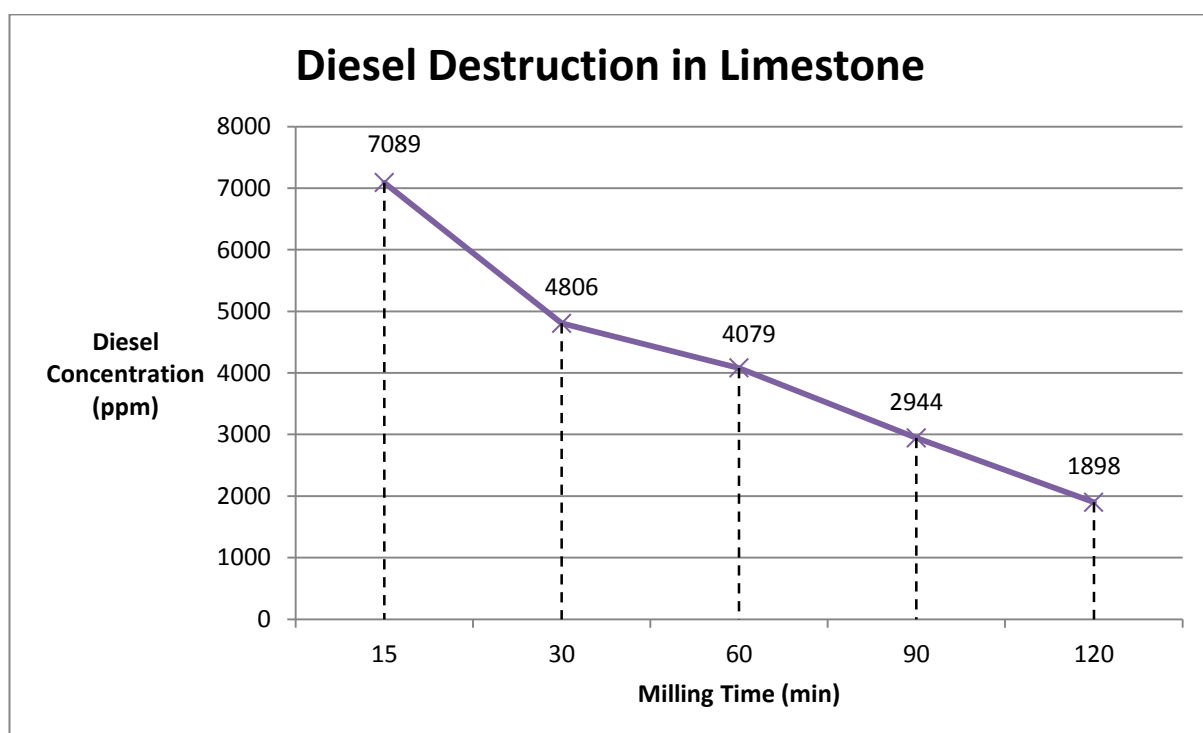
6.5.3 Scoria Diesel Trial

Diesel Destruction in Scoria
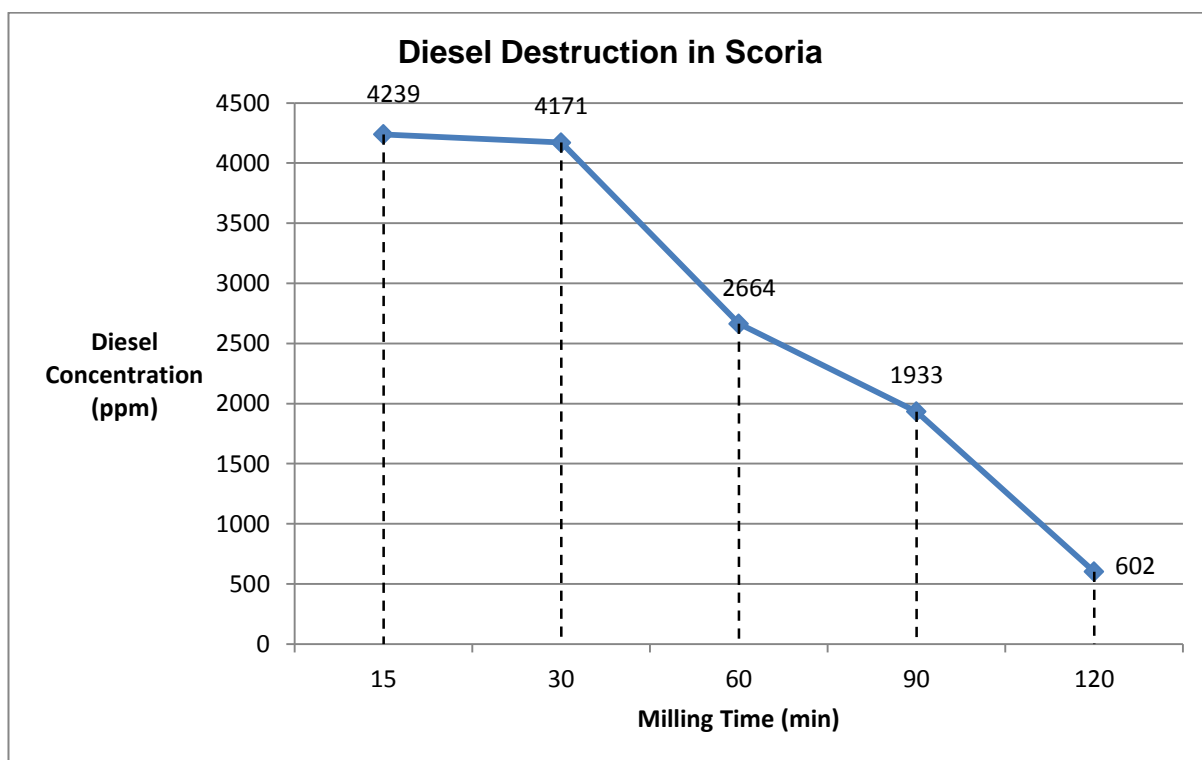
6.5.4 Subsoil Diesel Trial

Diesel Destruction in Subsoil
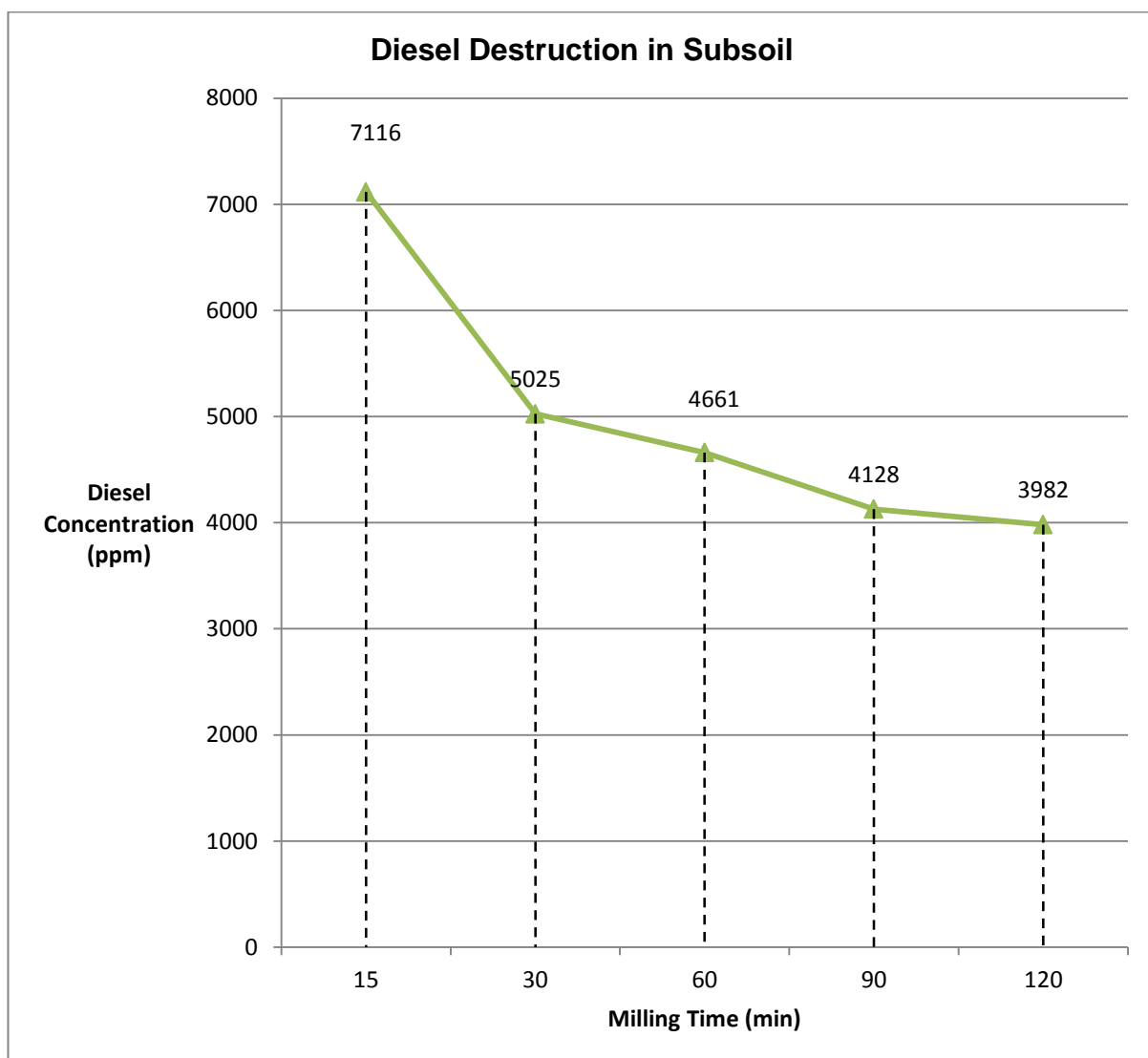
6.5.5 Discussion of Diesel Trials

Milling Interval (min)	Limestone Diesel Conc. (ppm)	Limestone Destruction Rate (%)
0	10000	0
15	7089	29
30	4806	52
60	4079	59
90	2944	71
120	1898	81

Milling Interval (min)	Quartz Diesel Conc. (ppm)	Quartz Destruction Rate (%)
0	10000	0
15	4351	56
30	3474	65
60	2382	76
90	1033	90
120	528	95

Milling Interval (min)	Scoria Diesel Conc. (ppm)	Scoria Destruction Rate (%)
0	10000	0
15	4239	58
30	4171	58
60	2664	74
90	1933	81
120	602	94

Milling Interval (min)	Subsoil Diesel Conc. (ppm)	Subsoil Destruction Rate (%)
0	10000	0
15	7116	29
30	5025	50
60	4661	53
90	4128	59
120	3982	60

Diesel Destruction in Different Soils

Diesel Destruction Rates in Different Soils
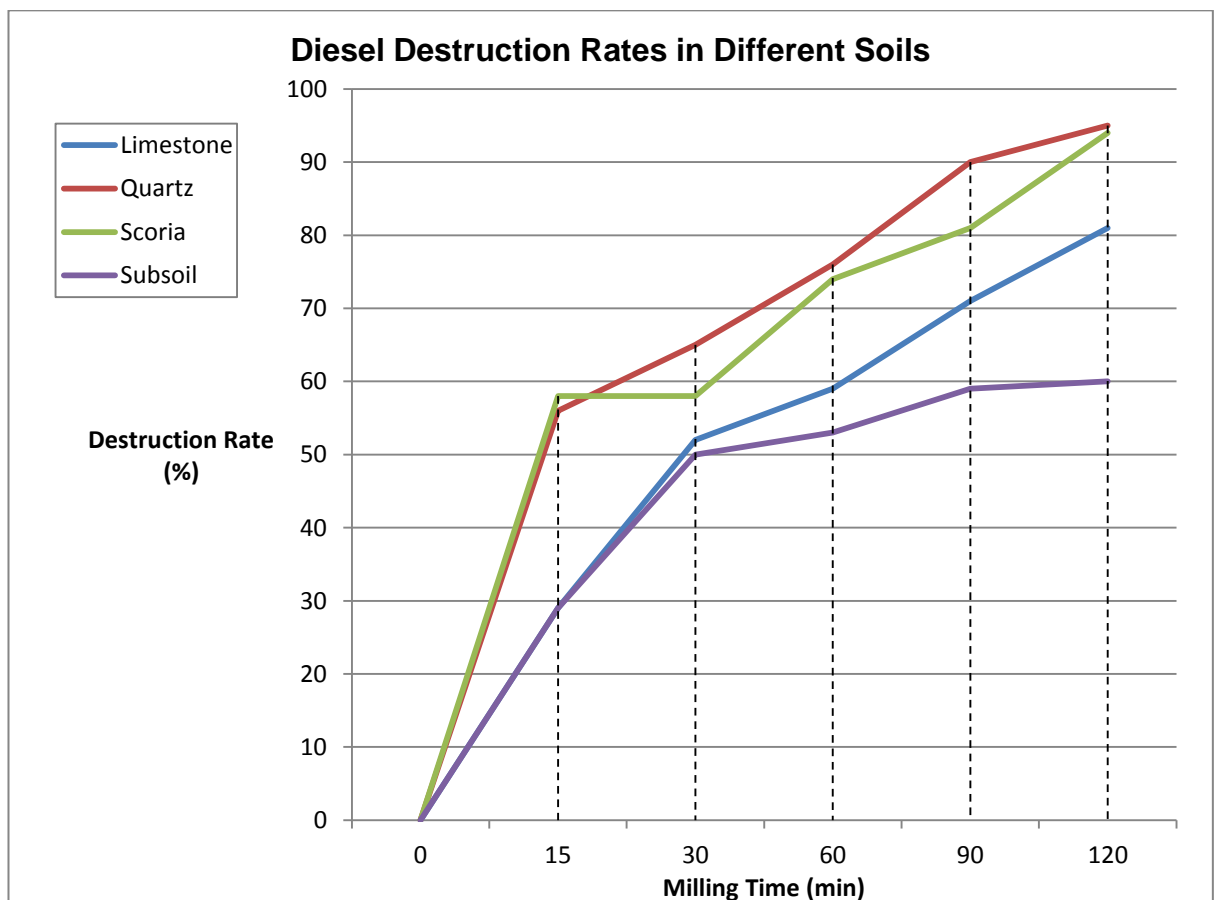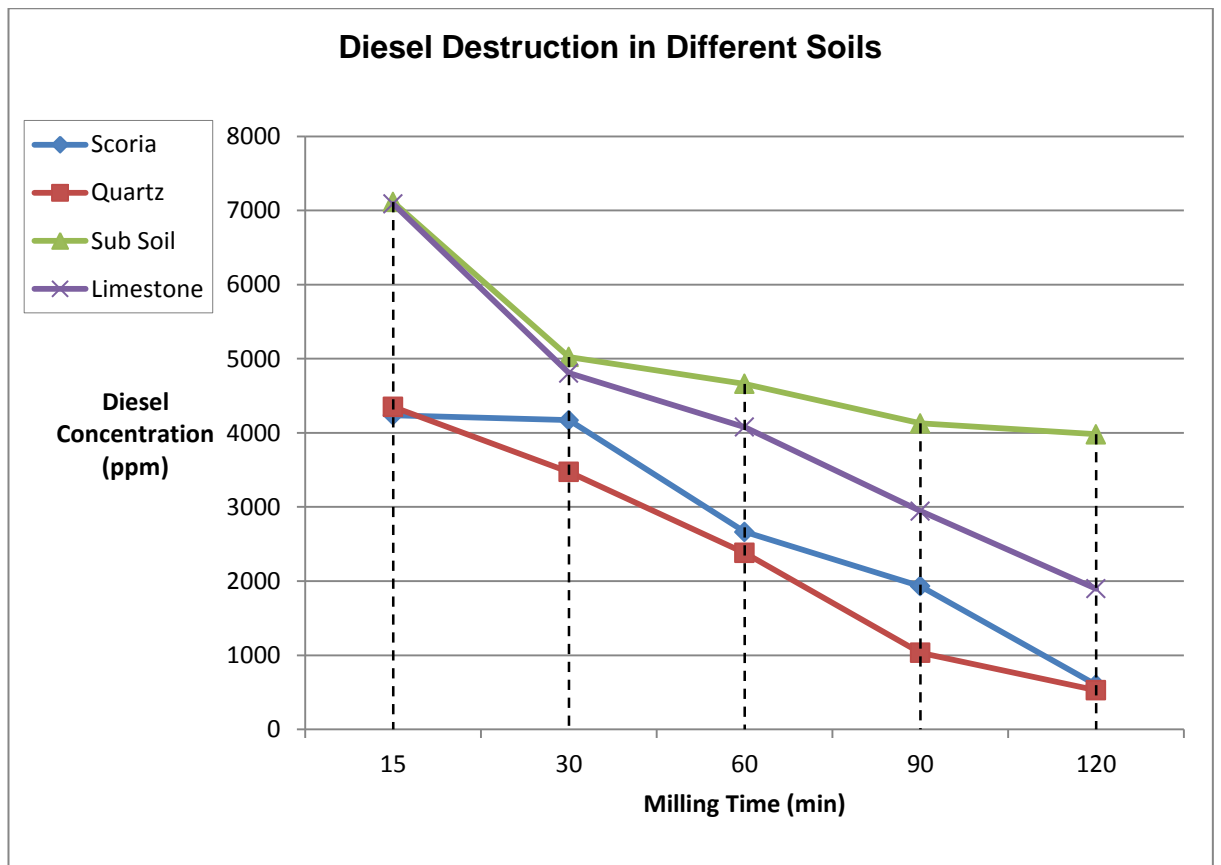
The diesel trials were conducted to study the behaviour of a complex hydrocarbon when subjected to the MCD process. Diesel is not a single molecule, but a mixture of saturated (60-80% of n-alkanes and naphthenes) and aromatic hydrocarbons. All the previous experiments used naphthalene as the organic pollutant analogue. Naphthalene is an aromatic hydrocarbon made up from a fused pair of benzene rings. Therefore, any reaction with just naphthalene unimolecular, making is a first-order reaction because the reaction only depends on the concentration of naphthalene.

Diesel was also chosen due to its high potential of being an environmental contaminant (Rosenberg 1996; Head 1999) as discussed in section 1.3.6. The initial concentration of diesel in this experiment was increased to 10,000ppm to simulate diesel spill or diesel leakage into subsoil from decrepit underground storage tanks (Hong 2010).
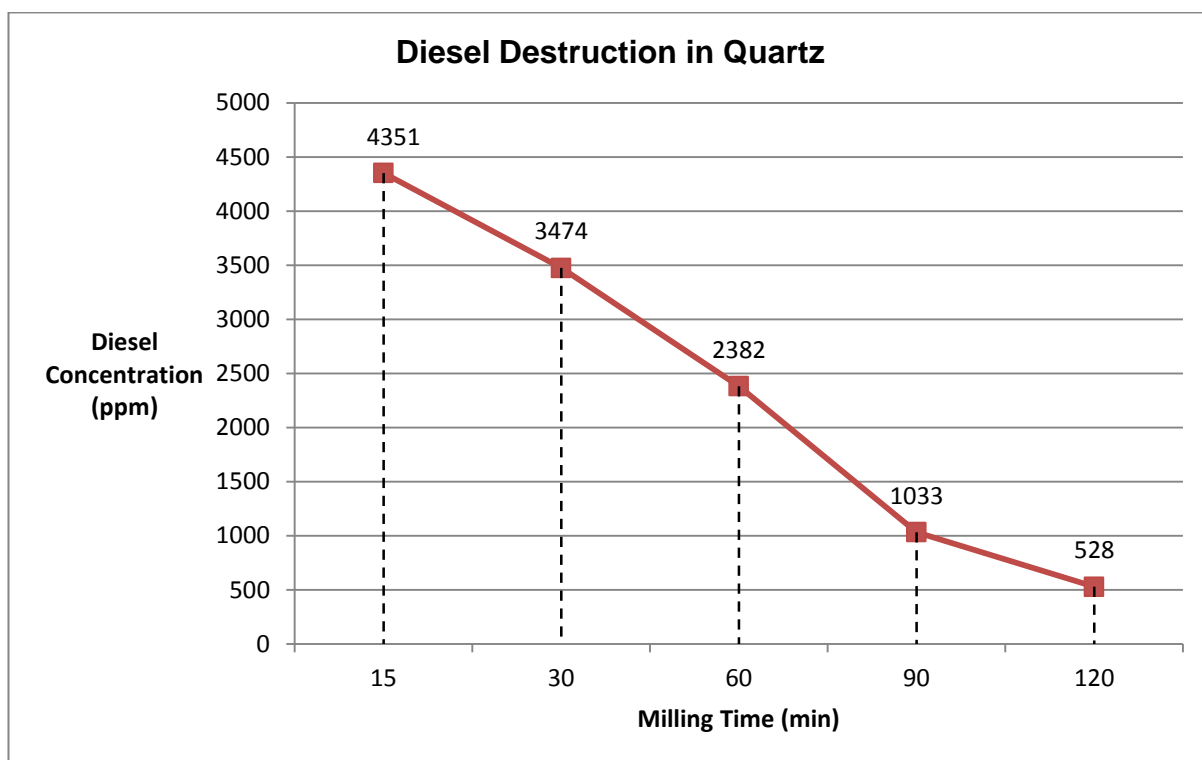
6.6 Halogenated Aromatic Hydrocarbon Trials

A study on the mechanochemical destruction of chloronaphthalene was carried out in four different soils. The four soils were limestone, quartz, scoria, and sub soil. Four 50 grams samples of each soil were measured out and 5,000ppm chloronaphthalene was added to each. Each sample was milled at intervals of 15, 30, 60, 90 and 120 minutes.

6.6.1 Limestone Chloronaphthalene Trial

Destruction efficiency of Chloronaphthalene in Limestone

A line chart plotting Concentration (pm) on the y-axis (0 to 4000) against Milling Time (min) on the x-axis (15, 30, 60, 90, 120). Data points: 3642 at 15 min, 3448 at 30 min, 2561 at 60 min, 1439 at 90 min, 1298 at 120 min.

6.6.2 Quartz Chloronaphthalene Trial

Destruction efficiency of Chloronaphthalene in Quartz

A line chart plotting Concentration (pm) on the y-axis (0 to 1400) against Milling Time (min) on the x-axis (15, 30, 60, 90, 120). Data points: 1208 at 15 min, 649 at 30 min, 33 at 60 min, 0.5 at 90 min, 0.3 at 120 min.

6.6.3 Scoria Chloronaphthalene Trial

Destruction efficiency of Chloronaphthalene in Scoria

Concentration (pm)

1874
1155
45
6
1

Milling Time (min)

15   30   60   90   120

6.6.4 Sub Soil Chloronaphthalene Trial

Destruction efficiency of Chloronaphthalene in Sub Soil

Concentration (pm)

4611
3209
2854
2472
1233

Milling Time (min)

15   30   60   90   120

6.6.5 Discussion of Chloronaphthalene Trials

Milling Interval (min)	Limestone Chloronaphthalene Conc. (ppm)	Limestone Destruction Rate (%)
0	5000	0
15	3642	27
30	3448	31
60	2561	49
90	1439	71
120	1298	74
Milling Interval (min)	Quartz Chloronaphthalene Conc. (ppm)	Quartz Destruction Rate (%)
0	5000	0
15	1208	76
30	649	84
60	33	99
90	0.5	100
120	0.3	100
Milling Interval (min)	Scoria Chloronaphthalene Conc. (ppm)	Scoria Destruction Rate (%)
0	5000	0
15	1874	63
30	1155	77
60	45	99
90	6	100
120	1	100
Milling Interval (min)	Subsoil Chloronaphthalene Conc. (ppm)	Subsoil Destruction Rate (%)
0	5000	0
15	4611	8
30	3209	36
60	2854	43
90	2472	51
120	1233	75

Destruction efficiency of Chloronaphthalene in Different Soils

Chloronpahthalene Destruction rate in Different Soils
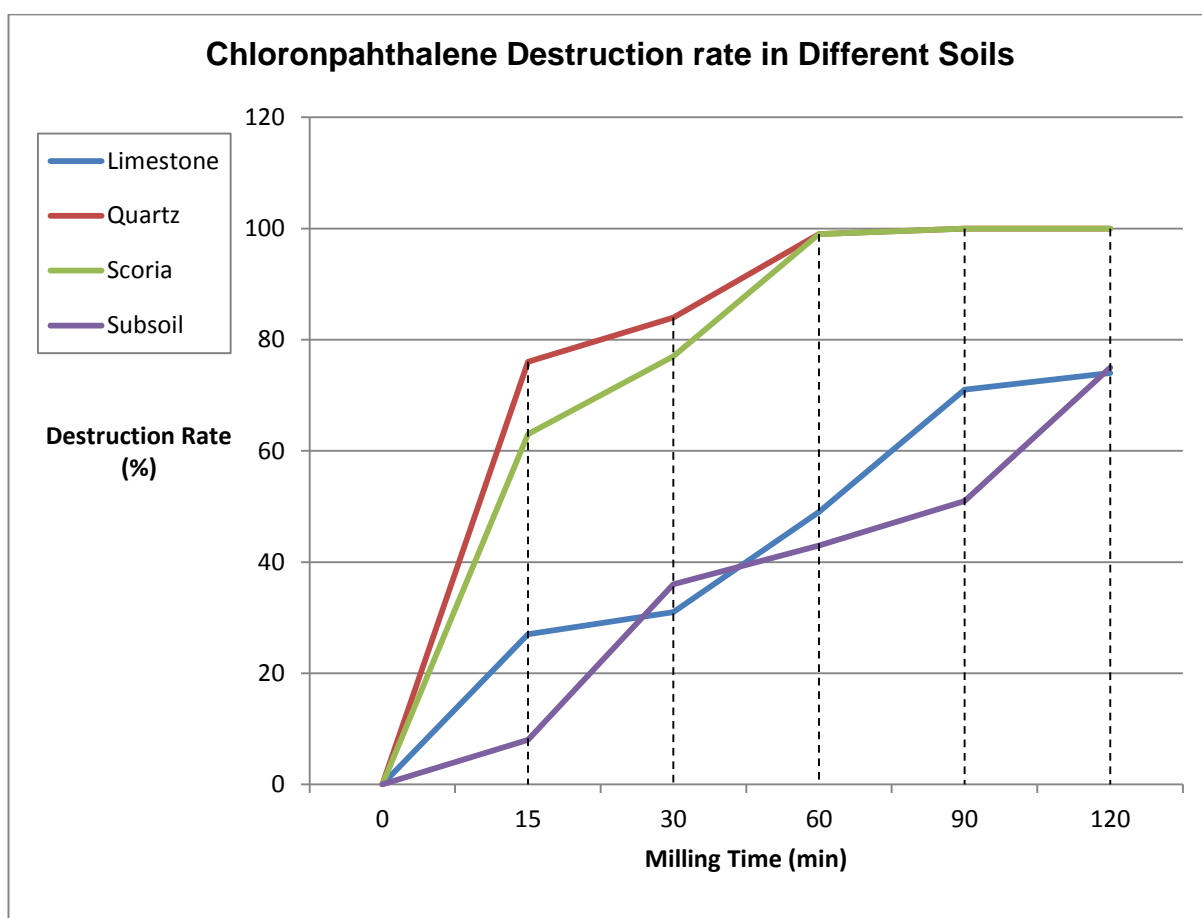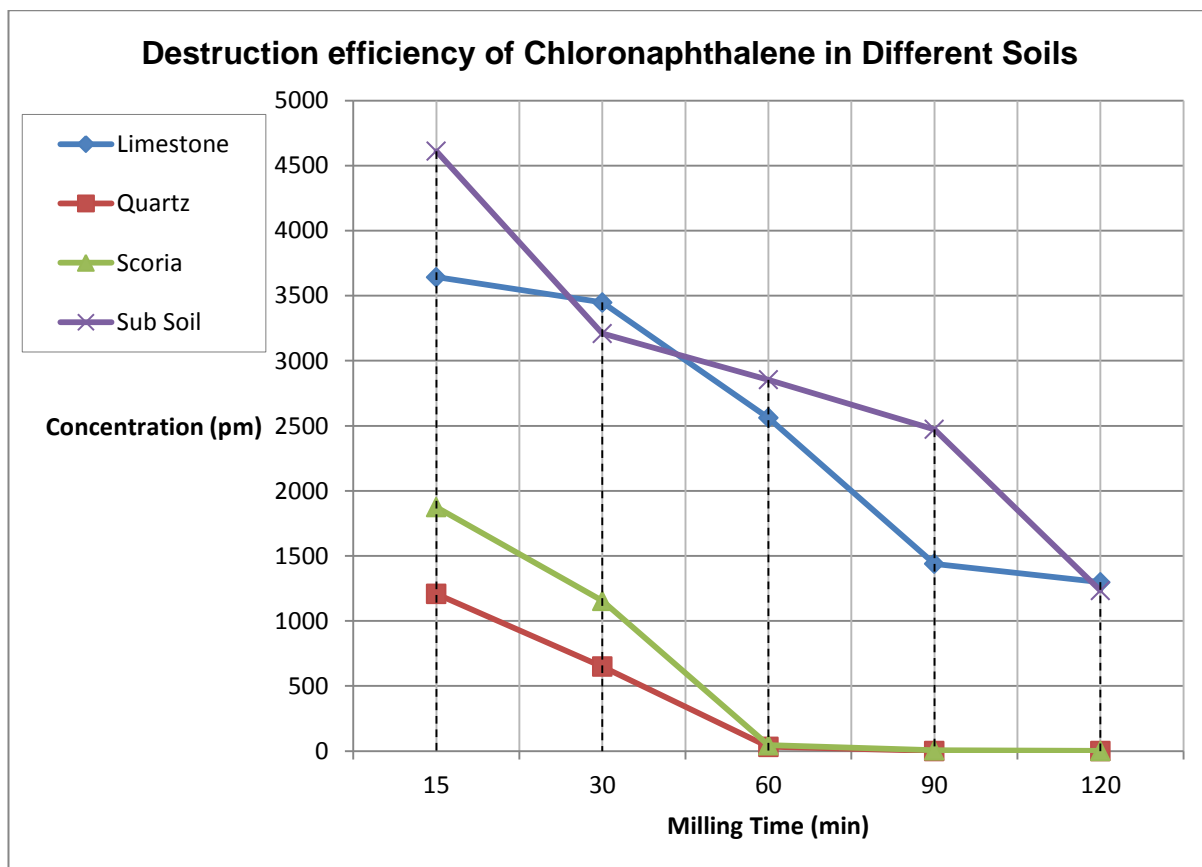
Chloronaphthalene was used to study dehalogenation of chlorinated organic pollutants by the MCD process. Many of the organic pollutants from pesticides to industrial by products are chlorinated e.g. 2,4,5-T,PCP, DDT etc., therefore it was important to understand how dehalogenation reactions behave in different soil types.

The destruction trends followed the pattern seen throughout this experiment. The drier, harder soil matrices i.e. quartz and scoria had a greater destruction rate than the softer, wetter soils i.e. limestone and subsoil.

Chloronaphthalene reached negligible levels in both quartz and scoria by the 60 minute milling interval. As far as remediation of land contaminated by a chlorinated organic pollutant, these levels are considered excellent. By the end of the milling cycle, there was virtually no chloronaphthalene in either soil.

The destruction rate of chloronaphthalene in limestone and subsoil was not as high. This is due to the soft nature of the two soils and particularly due to their relatively high water content. In the case of subsoil, it had a further disadvantage of containing clay. This further hindered the destruction of chloronaphthalene as evidenced in the graphs above.

It would seem that the type of soil does dictate the destruction rate of chloronaphthalene as it did with naphthalene, but as the milling continues the destruction rates increase. In a real world scenario chlorinated organic pollutants would be successfully destroyed with increased milling times.

6.7 Milling Jar Iron Test

During all the milling experiments, the colour of all the soil matrices developed red colouration when subjected to the extraction process. The extraction process was extracting something from the milled soils which gave the otherwise clear solution a red colour. The red colour would become darker and more prominent when extracting soils that have been milled for a long time i.e. the 90 and 120 minute milling intervals (fig. 6.1). The red colouration was also much more prominent in the dried soils.
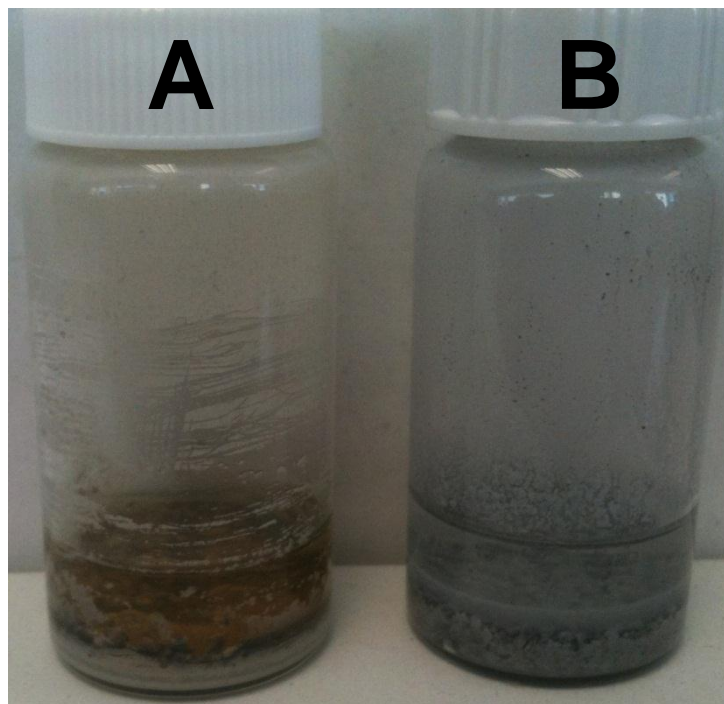

Figure 6.1 – 'A' Limestone milled for 90 minutes. 'B' Limestone milled for 15 minutes

It was hypothesised that iron from the grinding balls and jar were being introduced into the soil matrices during the milling process. It seemed logical that the longer the soil is milled, the more iron is imparted to it, hence the red colouration in only soils milled for longer periods.

To qualitatively determine the presence of iron, potassium thiocyanate was added directly into the sample and the red colour observed in the water layer.

For quantitative determination, spectrophotometry on the organic layer was performed. The organic layer was removed with a plastic dropper and 1 mL of 0.1% 1,10-phenanthroline and 0.5 mL of 1% hydroxylamine hydrochloride (to reduce all iron-III species to iron-II) together with 1 mL acetic acid buffer (pH of 4.6) were added into volumetric flask which then was diluted to the mark using deionised water.

While waiting for the sample to settle (over a period of 10 minutes), a standard solution series were prepared. Ferrous ammonium sulphate was used as the iron standard. Finally, both standards and samples were detected at the wavelength of 508 nm.

Atomic absorbance was also performed to determine the concentrations of iron within the milled soil. All the extraction solutions were filtered out into a new 20 mL glass test tube. 3mL 70% nitric acid was added followed by 7 mL DI water. Samples were then heated on water bath at around 70 °C to evaporate remaining organic solvents.

The iron concentration was determined by atomic absorbance under the following conditions:

- Oxidising acetylene/air flame.
- Absorbance wavelength of 283.3 nm.
- Lamp current of 5 mA.
- Integration time of 2 seconds.

6.7.1 Iron Spectrophotometry

Iron Calibration Standards

$y = 0.0455x - 0.0083$
$R^2 = 0.9924$

Absorbance (y-axis): 0, 0.1, 0.2, 0.3, 0.4, 0.5
Iron Concentration (ppm) (x-axis): 0, 2, 4, 6, 8, 10

Legend: ◆ Standards — Linear (Standards)

Iron Concentration vs Milling time

Iron Conc. (ppm) (y-axis): 6.00, 6.20, 6.40, 6.60, 6.80, 7.00, 7.20, 7.40, 7.60, 7.80, 8.00
Milling Time (min) (x-axis): 15, 30, 60, 90, 120

Data labels: 7.53, 7.58, 7.85, 6.70, 6.39
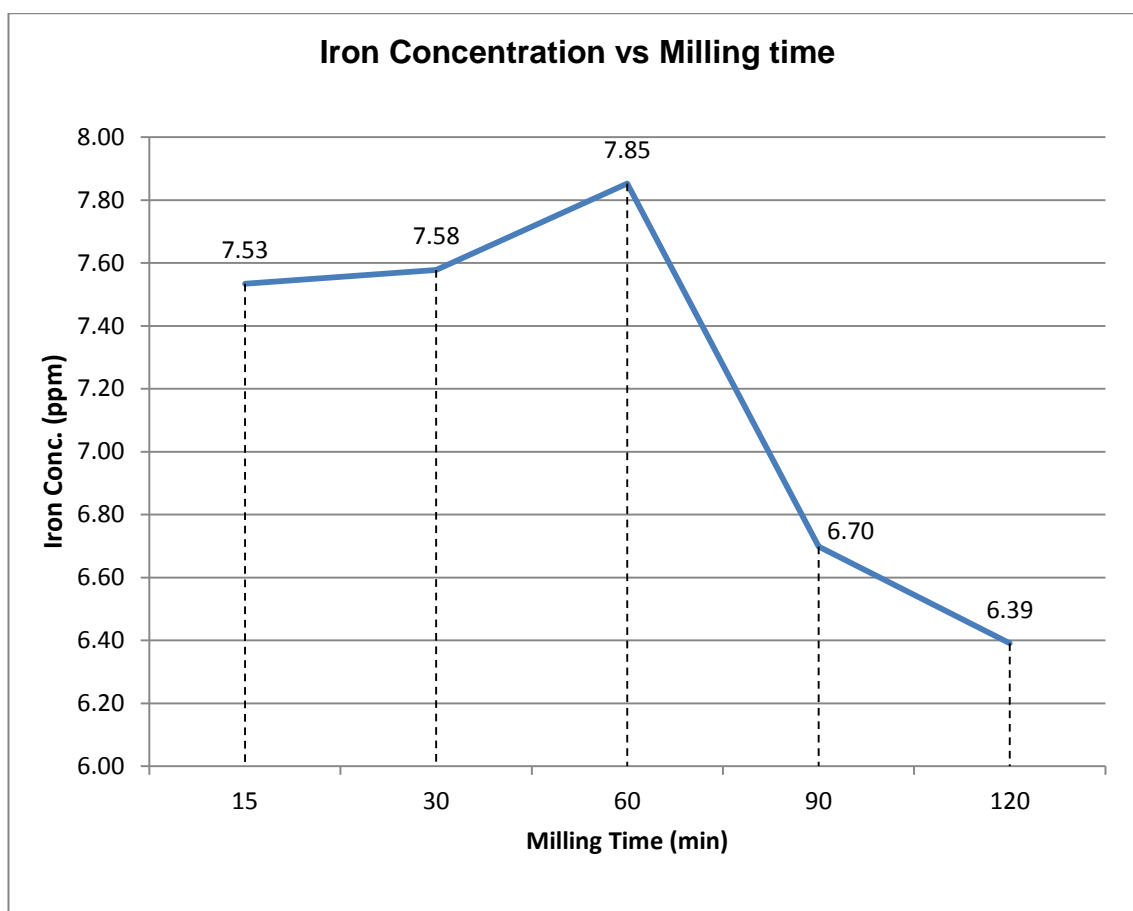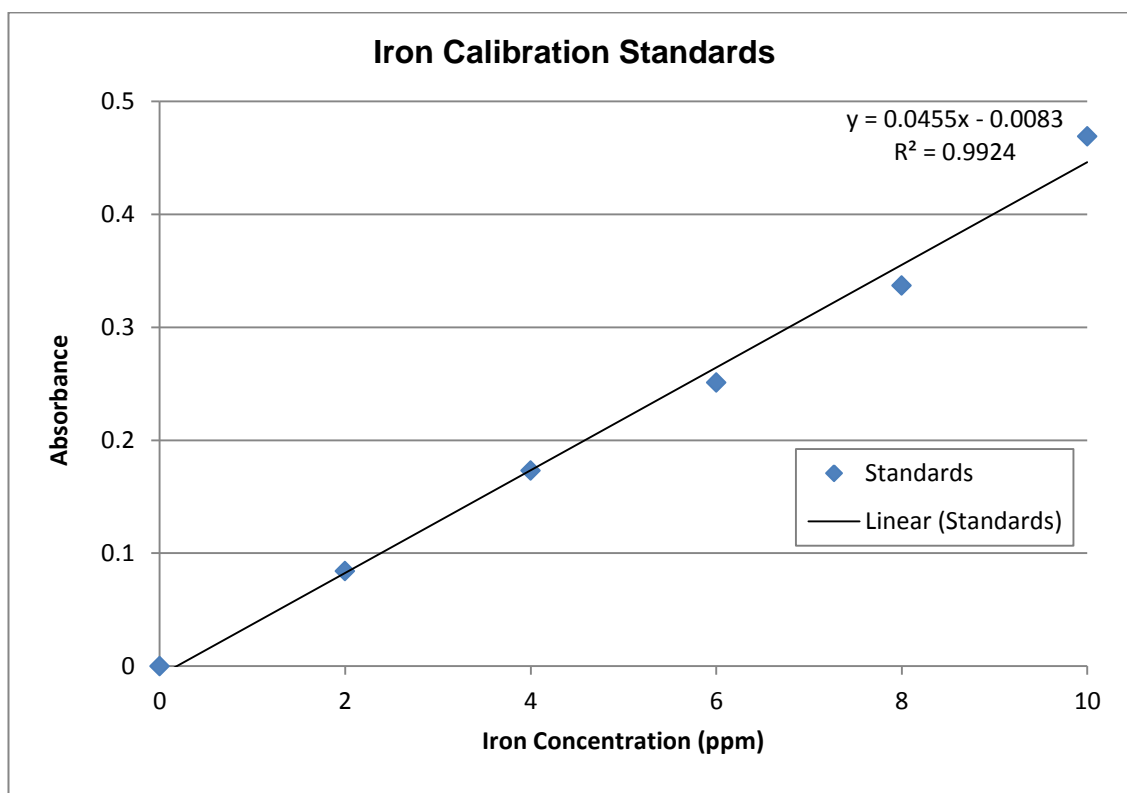
The iron concentrations were as follows:

Milling Time (min)	Iron Concentration (ppm)
15	7.53
30	7.58
60	7.85
90	6.70
120	6.39

The results obtained completely contradicted the hypothesis. Iron concentration initially increased during the 30 and 60 minute milling interval, but then dramatically decreased during the 90 and 120 minute milling intervals.

As mentioned in the organic matter milling experiments, sequestration would explain the decreasing iron concentrations, but does not offer an explanation for the red colouration exhibited in extractions of soil samples milled for 90 and 120 minutes.

6.7.2 Iron Atomic Absorbance

The iron concentrations were as follows:

Milling Time (min)	Absorbance	Concentration (ppm)
15	1.709	47
30	0.372	12
60	0.031	1
90	0.000	0
120	0.028	1

Iron Calibration Standards

$y = 0.0039x - 0.0004$
$R^2 = 0.9995$

Iron Concentration vs Milling Time
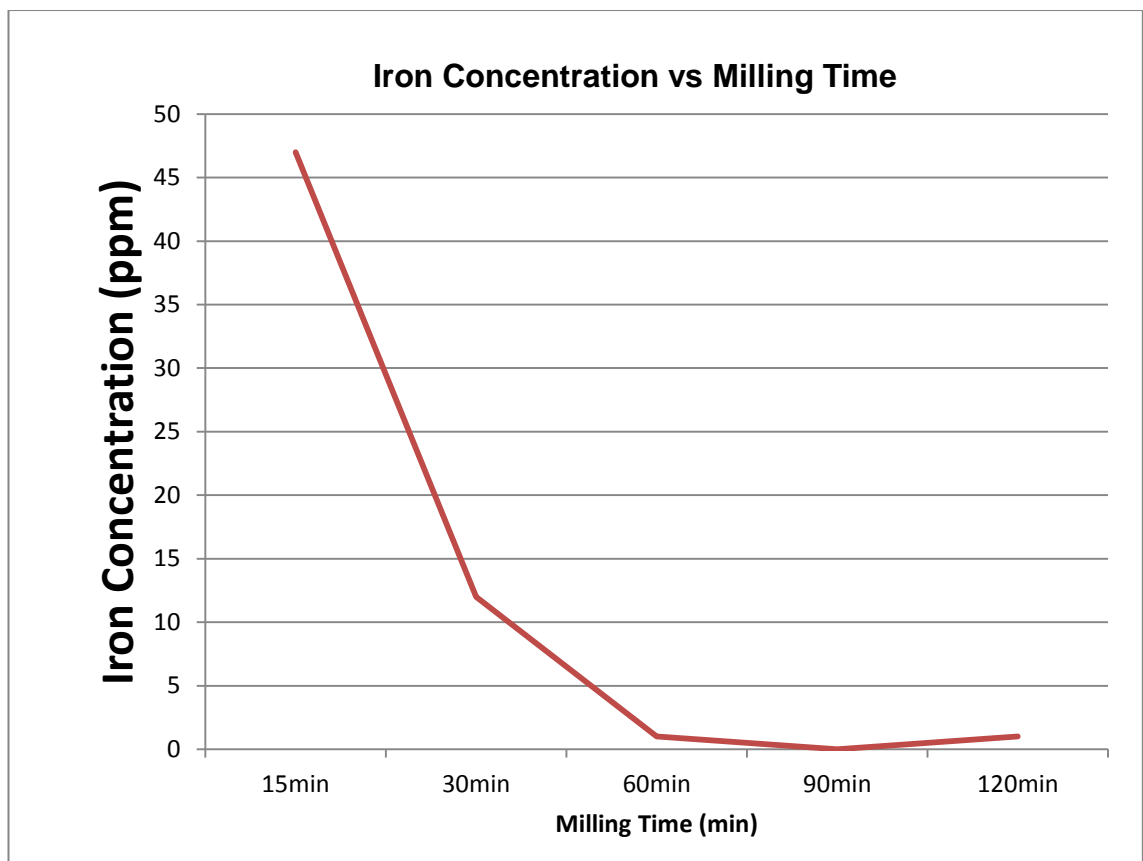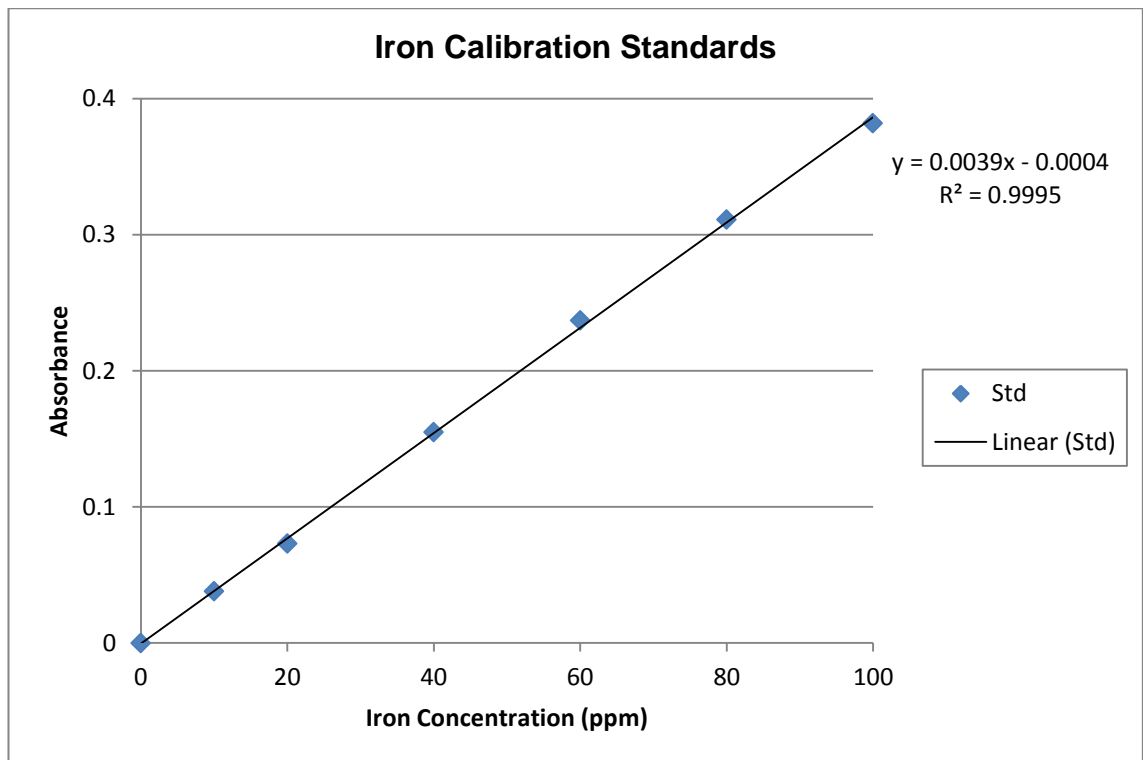
As in the spectrophotometry experiments, iron concentrations decrease as the

milling time increased.

6.8 Scanning Electron Micrographs of Milled Soils

A scanning electron microscope was used to study and image soils that have undergone milling. The aim was to see what physical changes happen to the soil when it is milled.

6.8.1 Scoria SEMs

30min
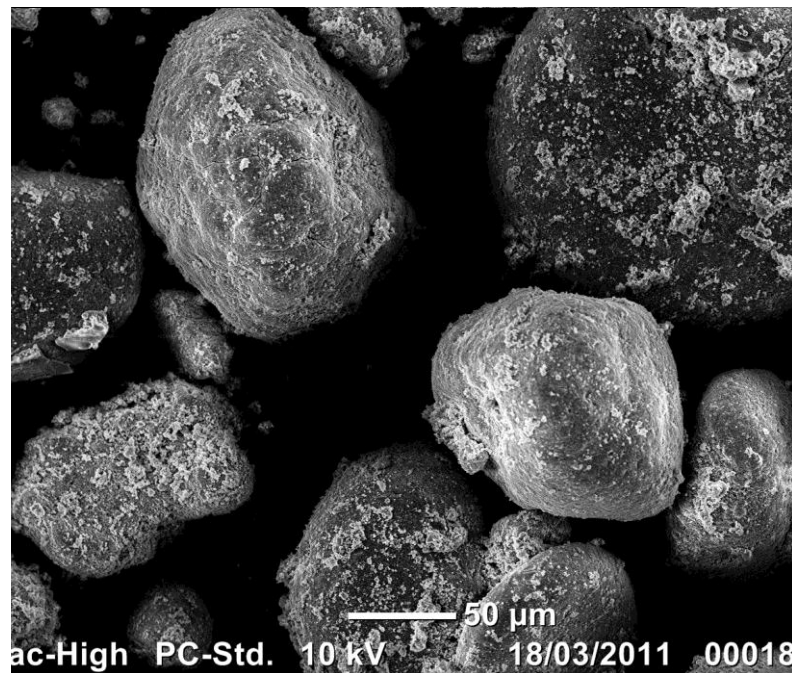
60min
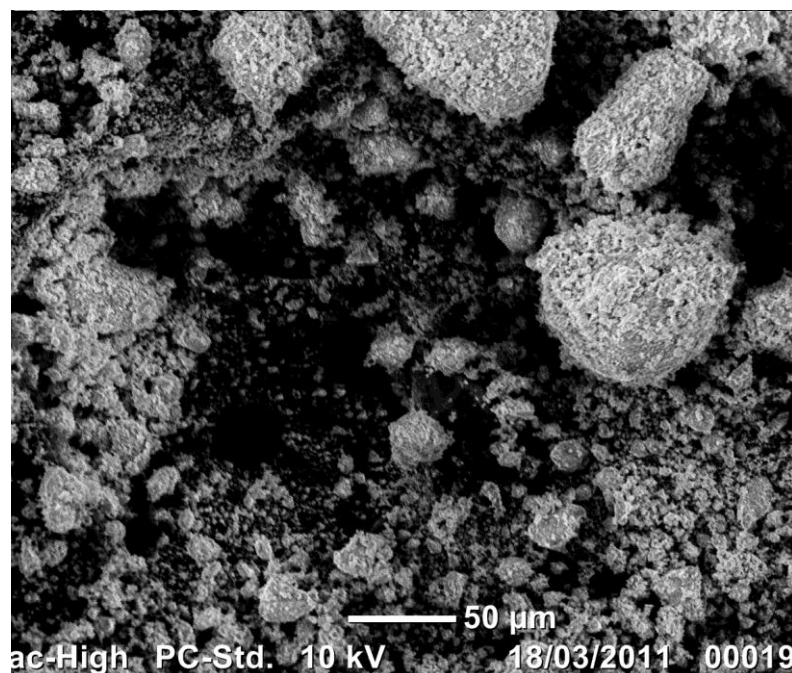
90min

120min

6.8.2 Sub Soil SEMs

30min

1.4 µm
0 º

5 µm

Vac-High   PC-Std.   10 kV   18/03/2011   000171

60min

1.2 µm
11º

Vac-High   PC-Std.   10 kV   x 3000   10 µm   000177

Vac-High PC-Std. 10 kV x 3000   10 µm   000180

Vac-High PC-Std. 10 kV   18/03/2011   000181

6.8.3 Clay SEMs

30min

5 μm

Vac-High   PC-Std.   10 kV   18/03/2011   000133

60min

5 μm

Vac-High   PC-Std.   10 kV   18/03/2011   000134

90min

5 µm

Vac-High   PC-Std.   10 kV   18/03/2011   000136

120min

5 µm

Vac-High   PC-Std.   10 kV   18/03/2011   000137
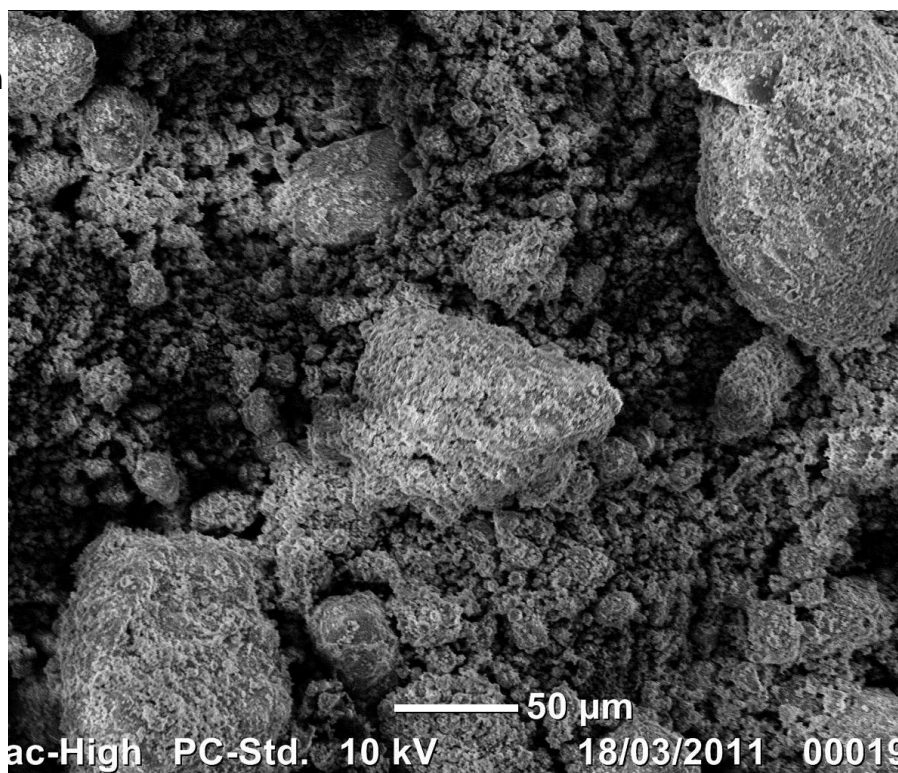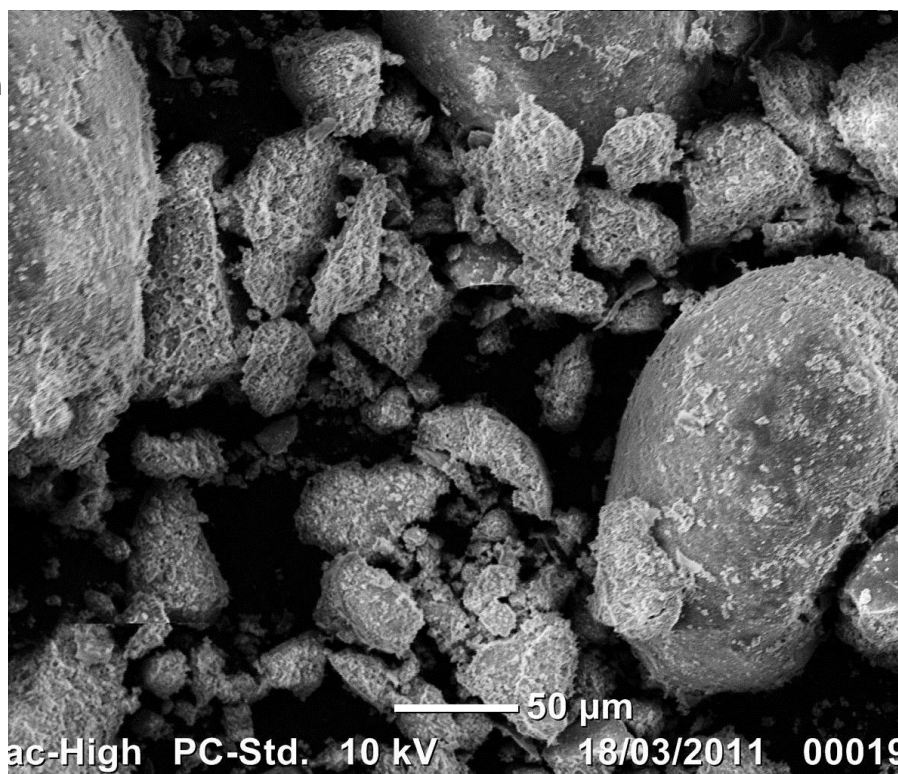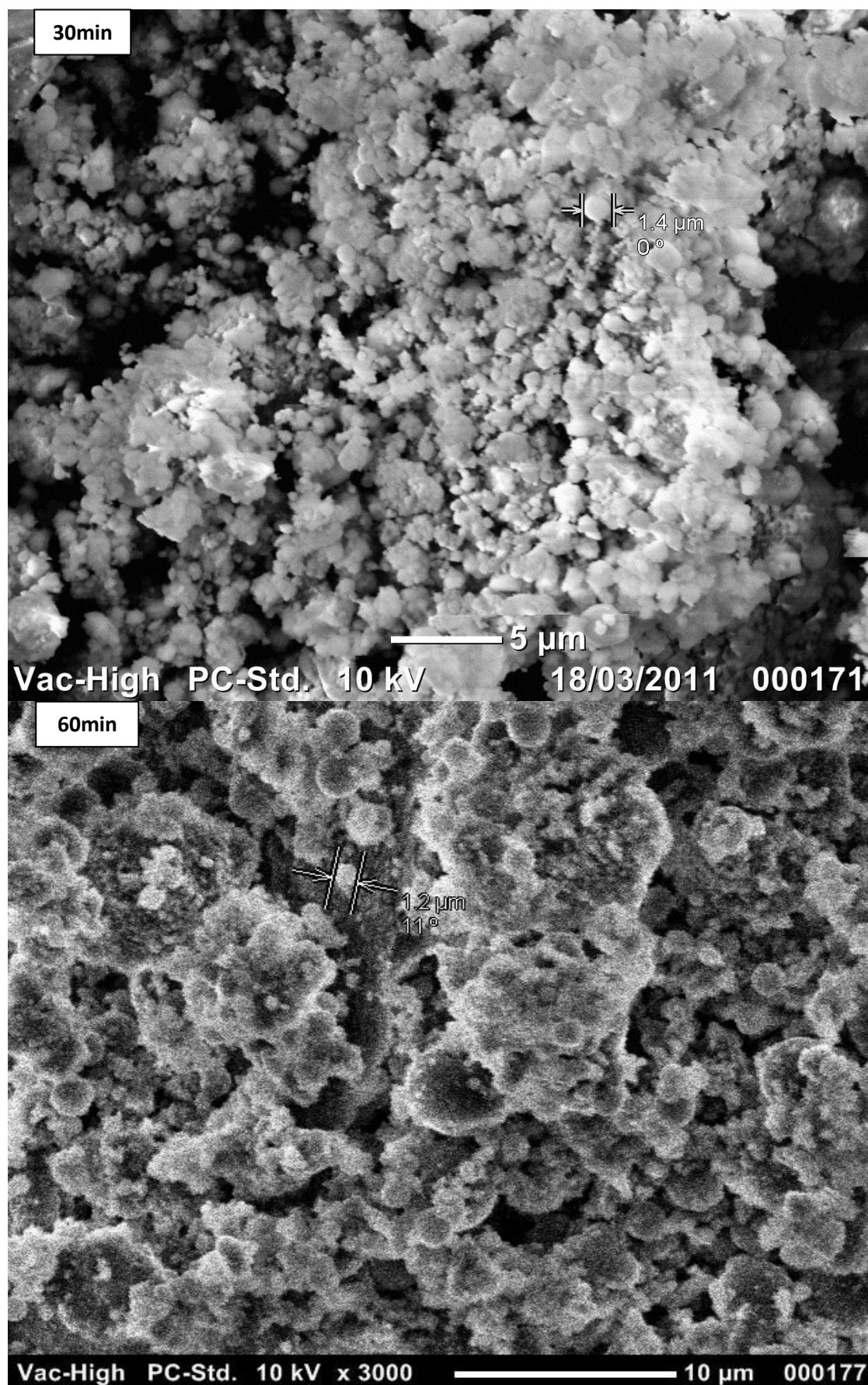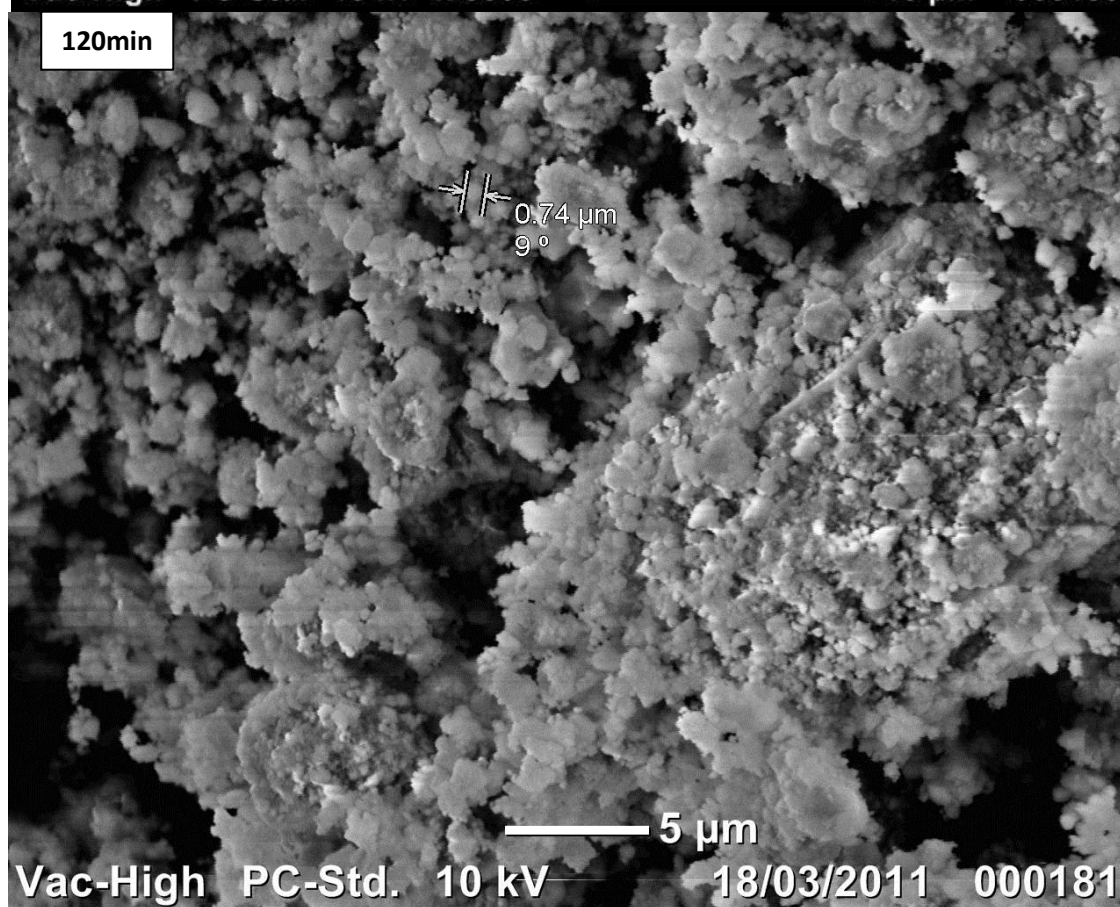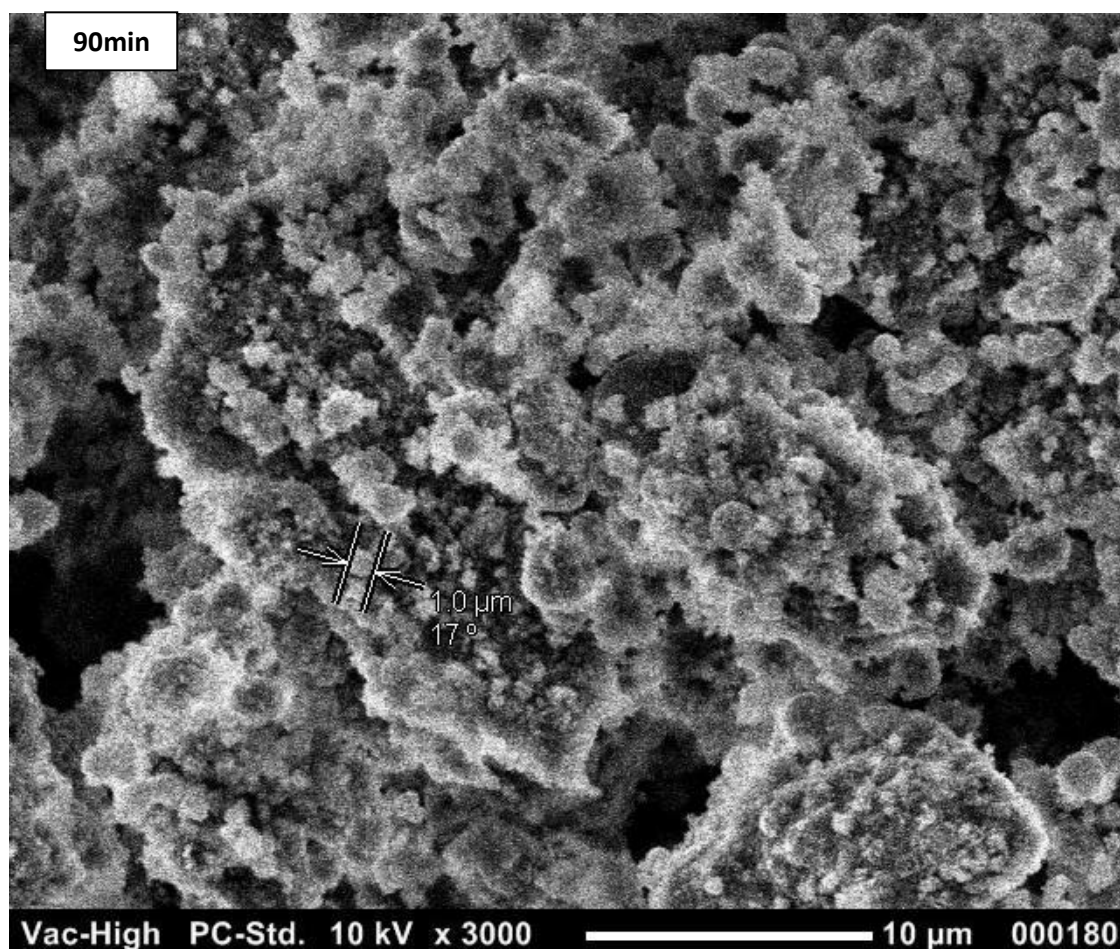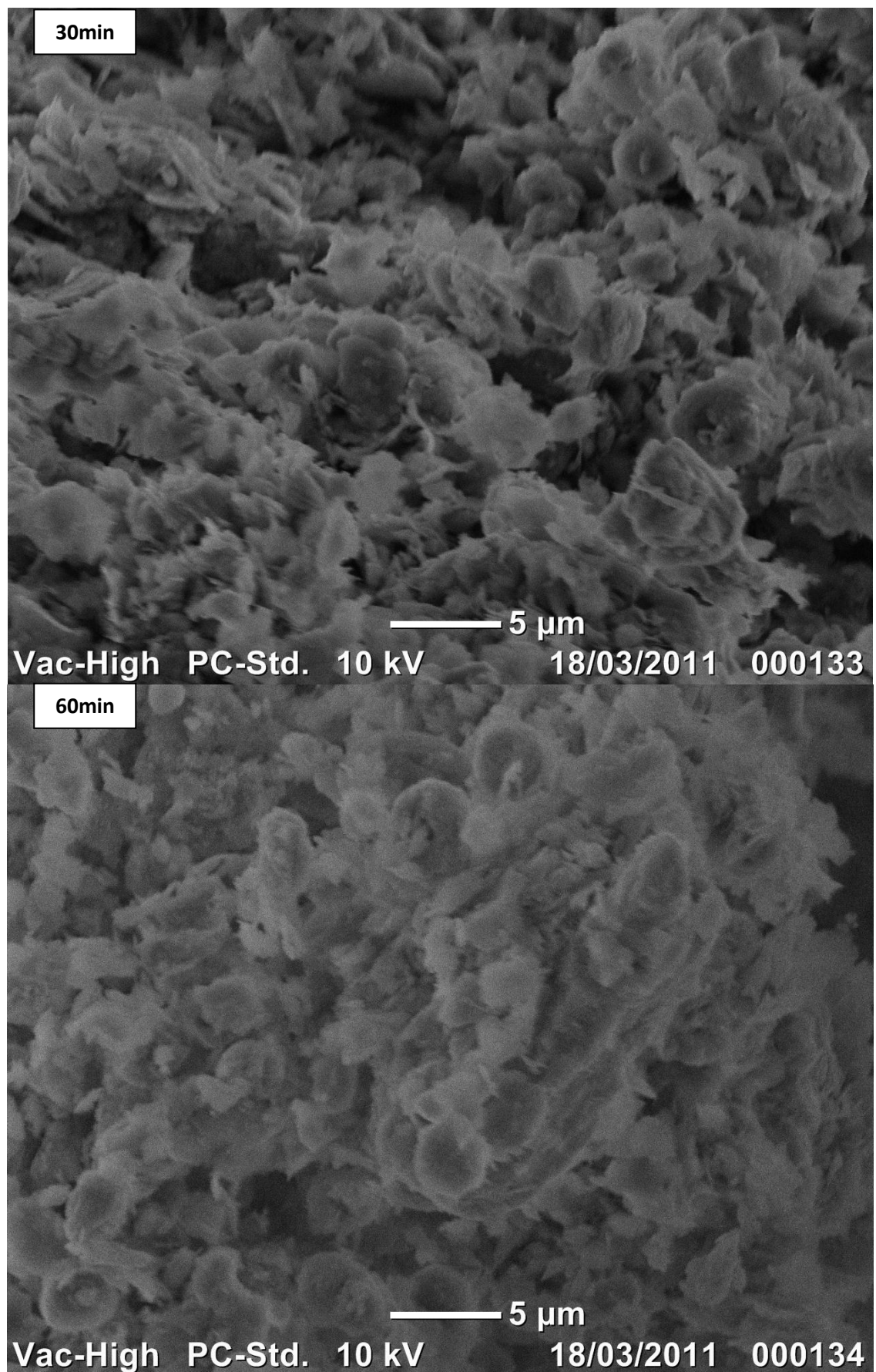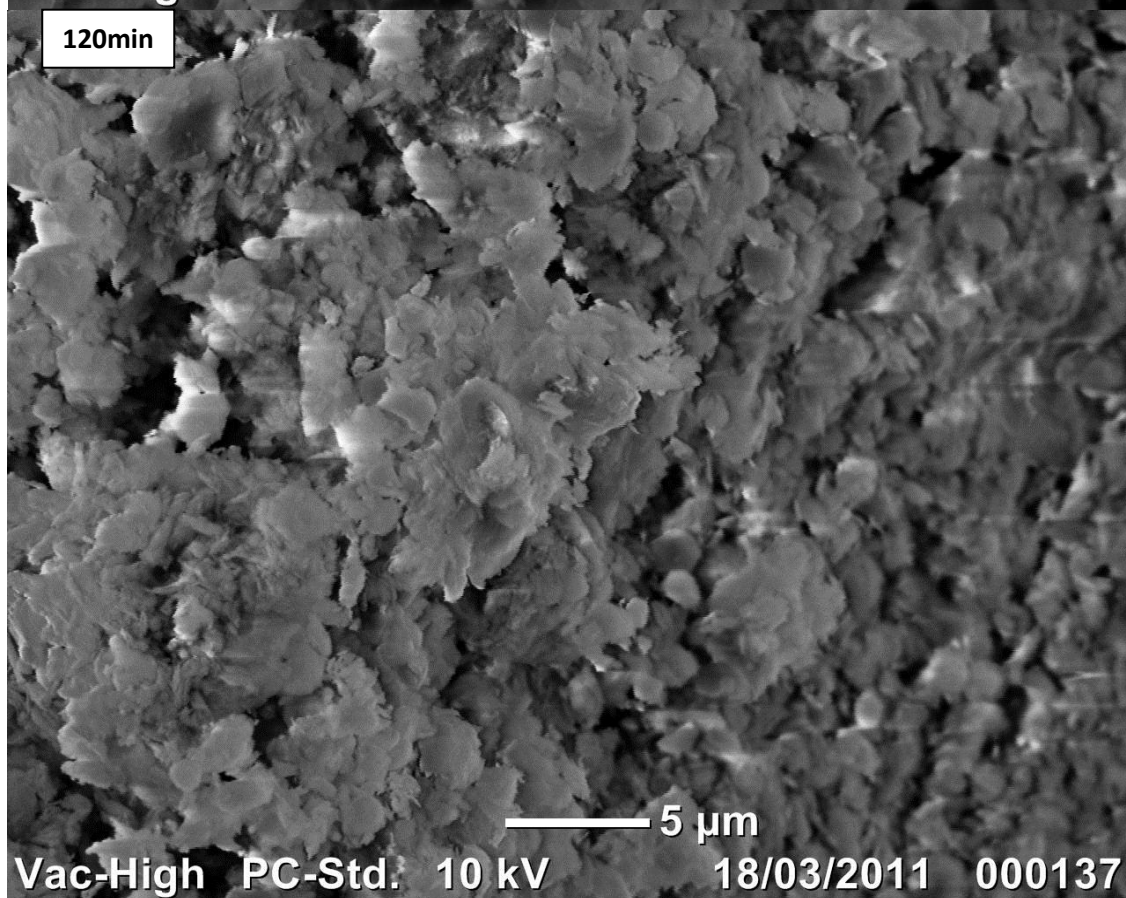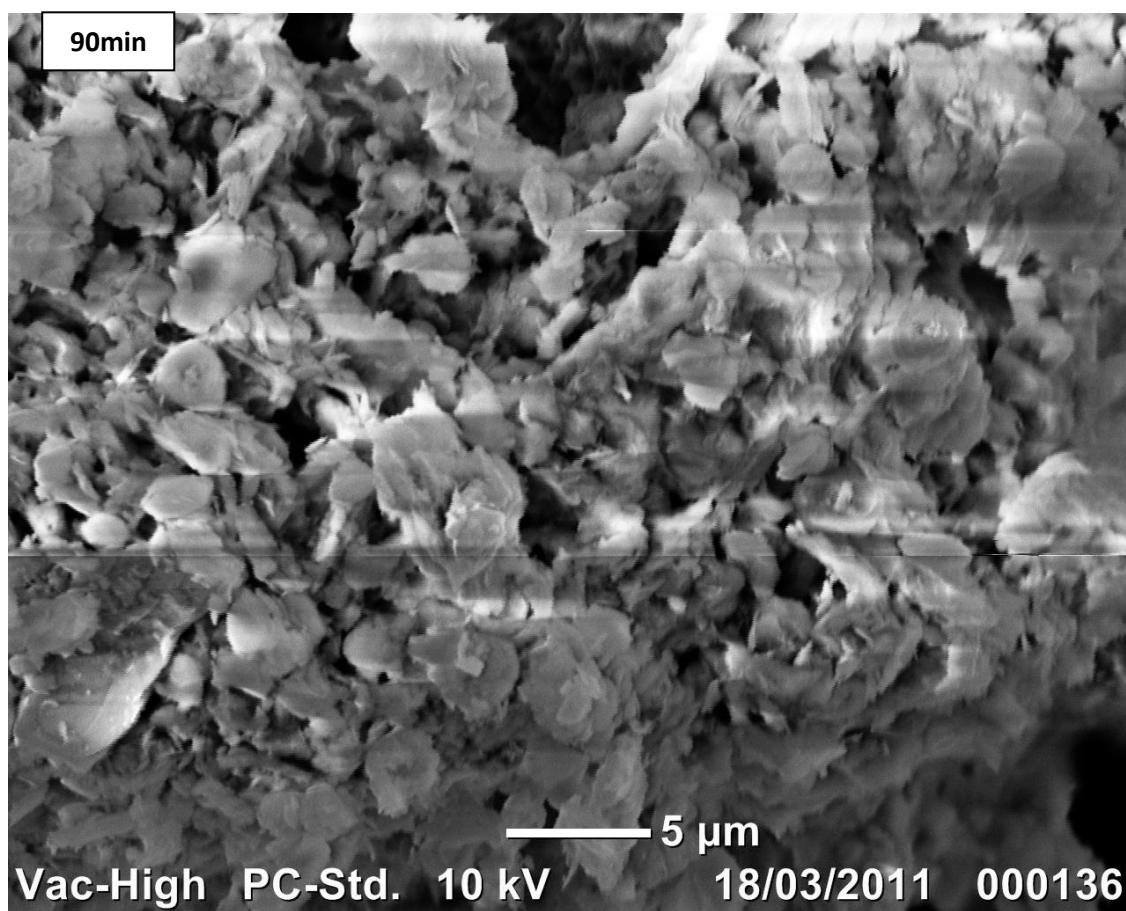
6.8.4 Clay Dried at 700°C SEMs

90min

Vac-High   PC-Std.   10 kV   18/03/2011   000153

120min

Vac-High   PC-Std.   10 kV   18/03/2011   000156
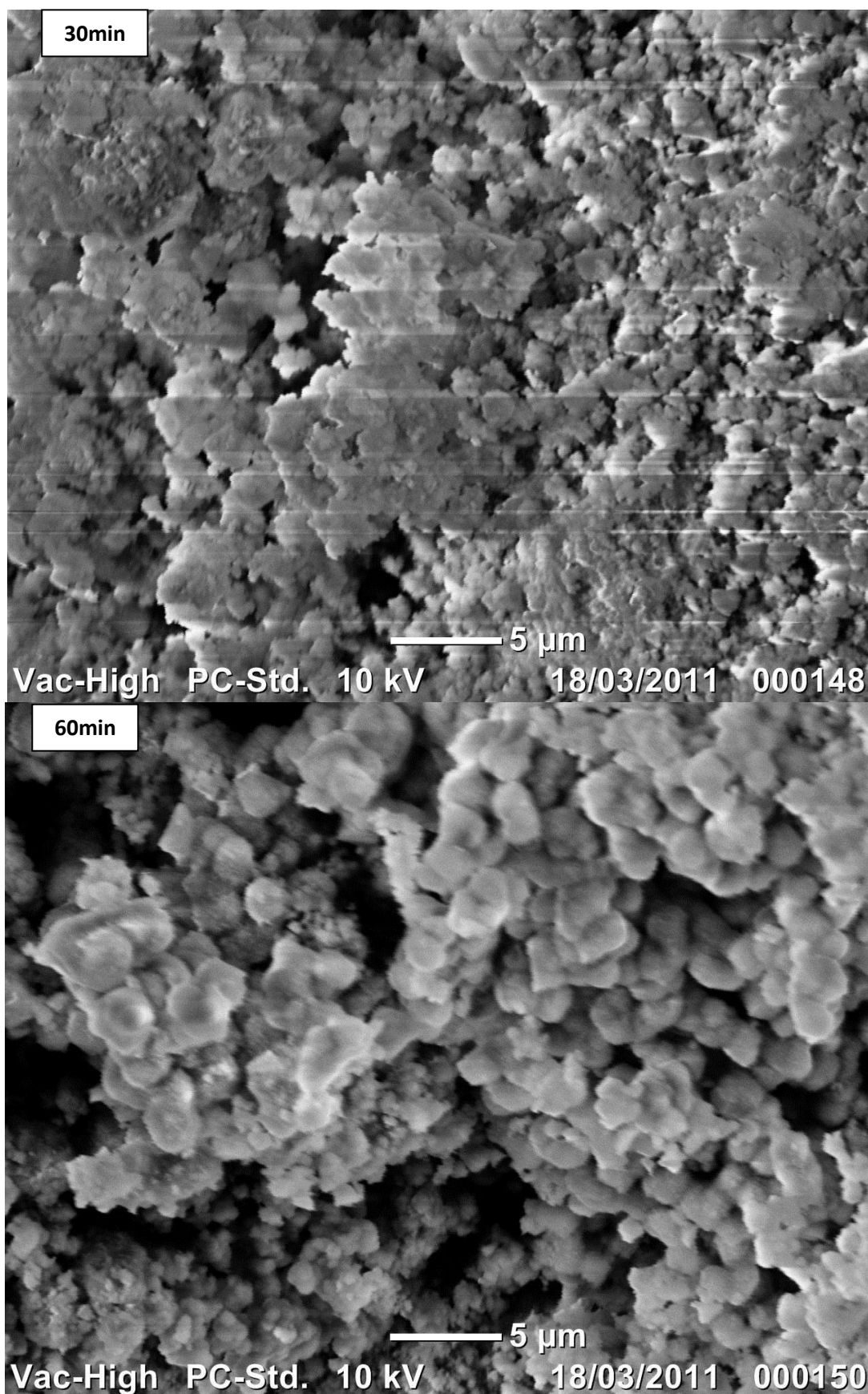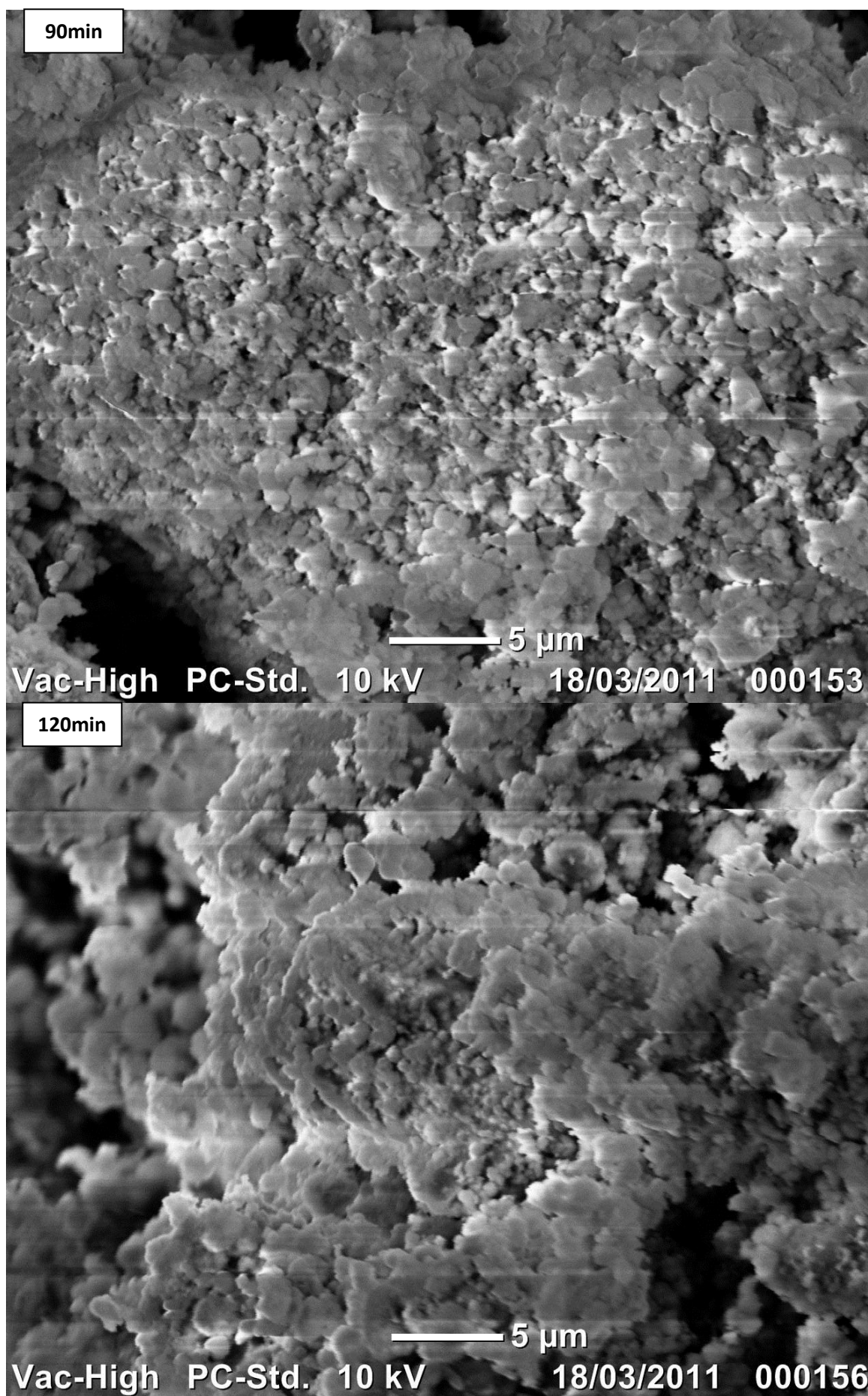
6.8.5 Quartz Scanning Electron Micrographs

30min

Vac-High   PC-Std.   10 kV   18/03/2011   000203

60min

Vac-High   PC-Std.   10 kV   18/03/2011   000205

90min

Vac-High PC-Std. 10 kV   18/03/2011   000207

120min

Vac-High PC-Std. 10 kV   18/03/2011   000209
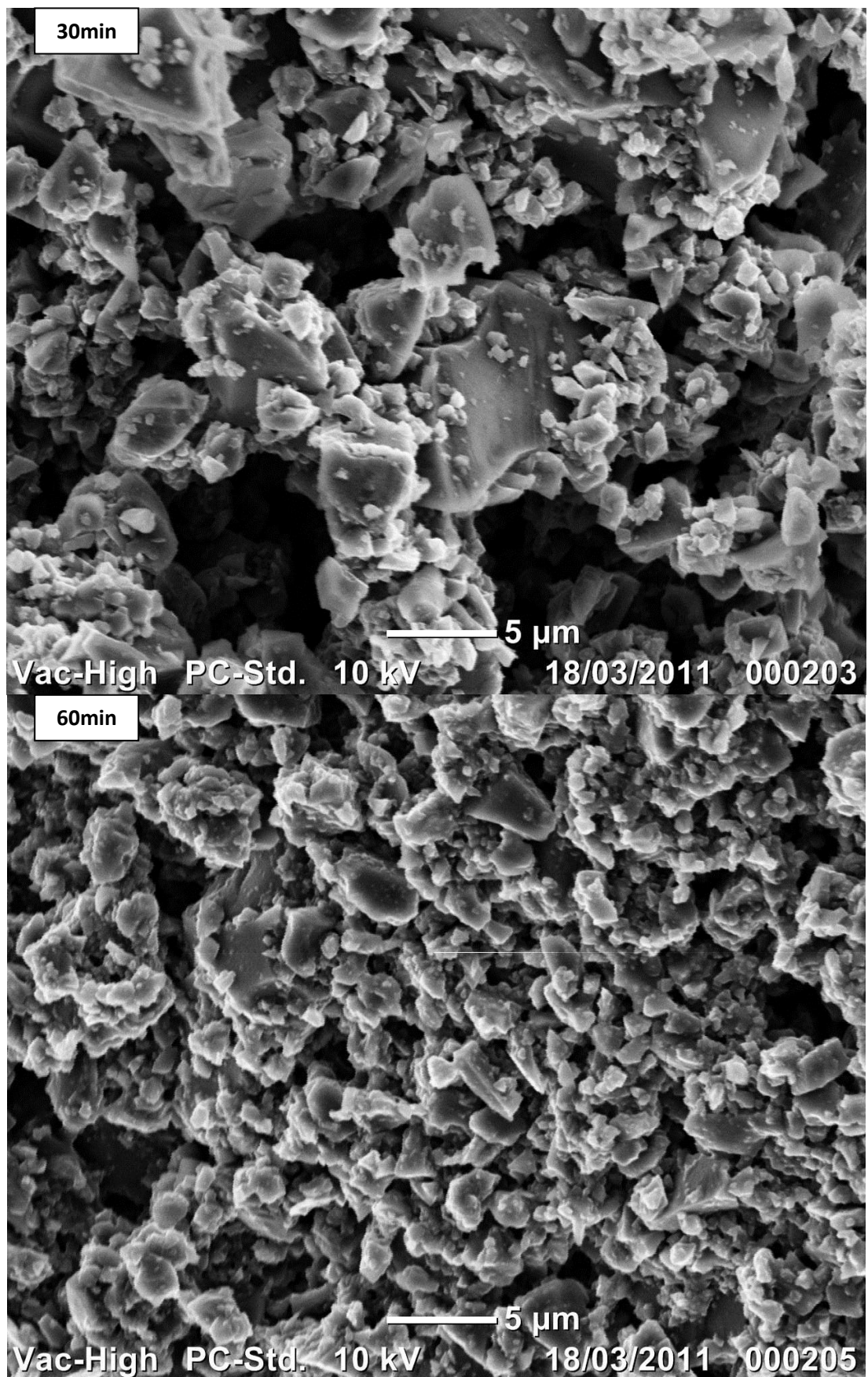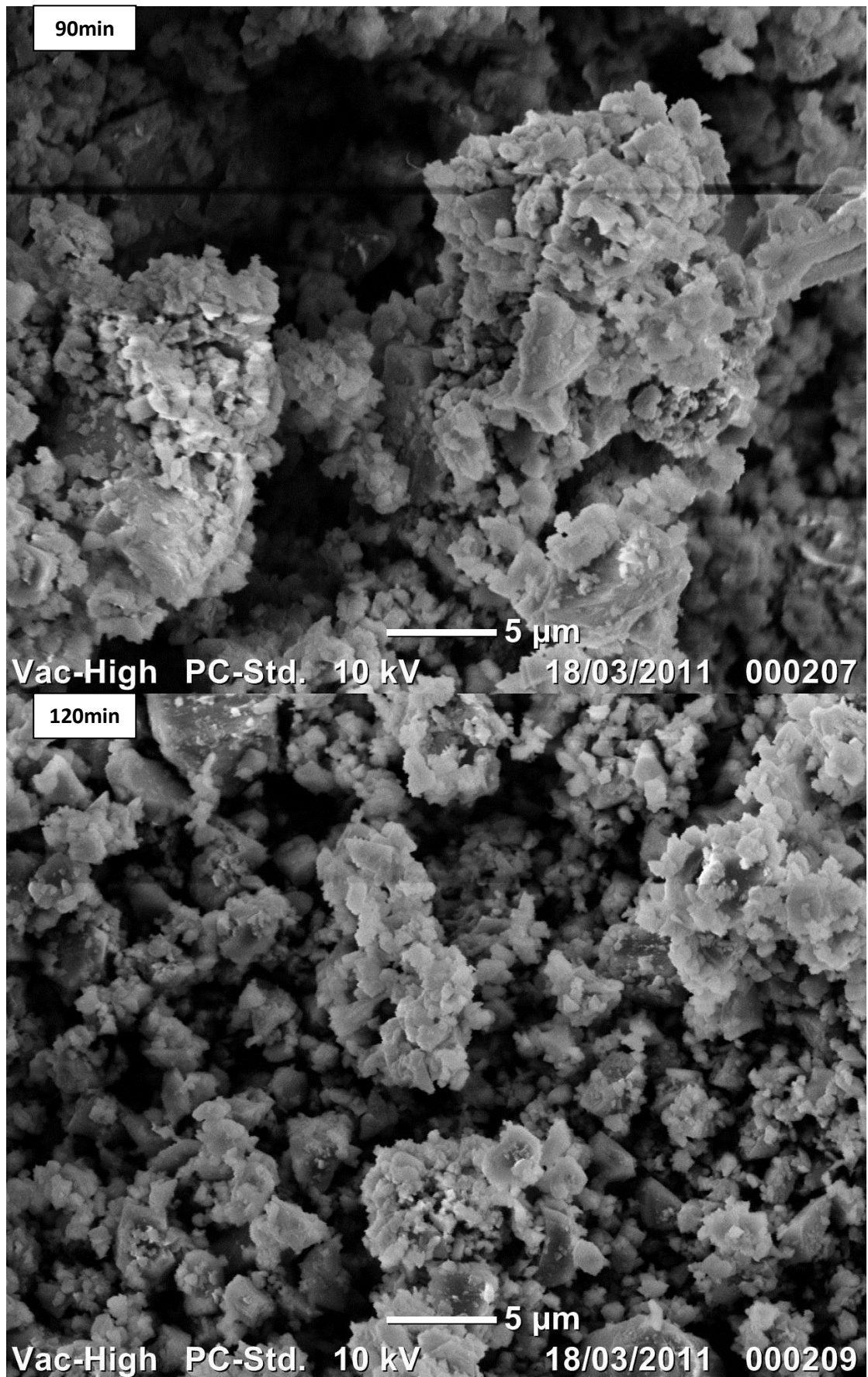
6.8.6 Discussion of Milled Soil Micrographs

The particle size of the scoria sample decreased from the 30 to 60 minute milling interval. The 90 minute milling sample scan had slightly bigger particles while the 120 minute milling sample scan had much bigger particle sizes compared to the 60 minute scan.

This pattern of initial decreasing followed by increasing of particle size has been documented in past articles.

In the initial stage of mechanochemical synthesis, particle size reduction and plastic deformation occurs at least to some extent before the chemical bonds are formed. The reduction of particle dimensions on size could be divided into three stages (Boldyrev 1971).

1. The first stage is characterised by a progressive decrease with milling time of the particle dimensions.
2. The second stage is characterised by the start of aggregation of the particles.
3. The third stage is characterised the establishment of an equilibrium, in which the particle dimensions remain generally unchanged with time. The specific surface area changes analogously.

There appears to be an important feature here. As the particle size is reduced, there is also an increase in plastic deformation of particles. Thus during milling the surface area not only increases but the surface contact is enhanced by the deformation of the particles. Boldyrev et. al (Boldyrev 2000) have pointed out that plastic deformation of one component or both the increasing of contact area is more important than the number of particles. This feature of increasing surface area is augmenting all the reactions and models discussed in chapter 3.

The subsoil particle sizes follow the same trend exhibited by scoria and by the study by Boldyrev et. al. There is an overall increase in particle size from the 30 to 60 minute milling interval. The Boldyrev model suggests that there is an initial decrease in particle size followed by an increase (aggregation) which is mirrored in the 30 and 60 minute milling interval micrographs respectively.

The particle sizes in the micrographs of the 90 and 120 minute milling interval have again decreased compared to the 60 minute particles. This would suggest that the particles have reached equilibrium as the particles in both the 90 and 120 minute micrographs are generally unchanged.

The undried clay scanning electron micrographs (SEMs) depicts a trend that did not follow the Boldyrev model; however their test soil was quartz only. There is a gradual reduction of undried clay particle size throughout the milling cycle. There is a characteristic feature in the undried clay of round and elliptical disks. The shapes of these disks decrease in size and become distorted as milling time increases. The chemical/structural composition and or the water content of clay must be having an effect on the particle size equilibrium.

The slower rate of particle size reduction in undried clay could be related to the decreased destruction rates of naphthalene as discussed in sections 5.1.9 and 5.2.1.7 due to the relationship of reaction rate and surface area. Boldyrev et. al determined that plastic deformation, decreasing of particle size i.e. increasing surface area is more important than the number of particles in a reactive milling context.

Dried clay was then examined to determine whether water was causing this irregular behaviour. It is clear from the SEMs that the water in the undried clay was causing the irregular trend. The dried clay particles in the 30 minute scan

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were smaller than the particles in the 60 minute scan. This would suggest that there was an initial reduction of particle size at 30 minutes, followed by aggregation of the particles at 60 minutes. The particles then decreased in size again during the 90 and still remained relatively unchanged after the 120 minute milling interval suggesting an arrival at equilibrium.

The quartz SEMs exhibited the exact trend suggested by Boldyrev; the particle sizes decreased during the 30 and 60 minute milling intervals followed by aggregation in the 90 minute interval. Particle size equilibrium was reached during the 120 minute milling interval.

6.9 SEMs of Quartz milled at 5min Increments

5min
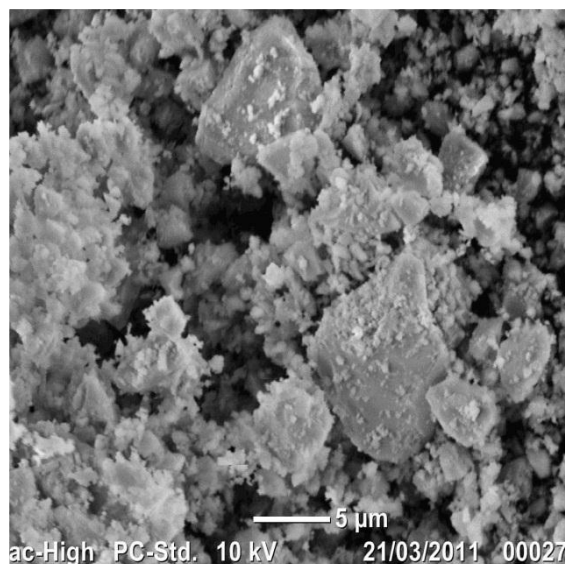
10min
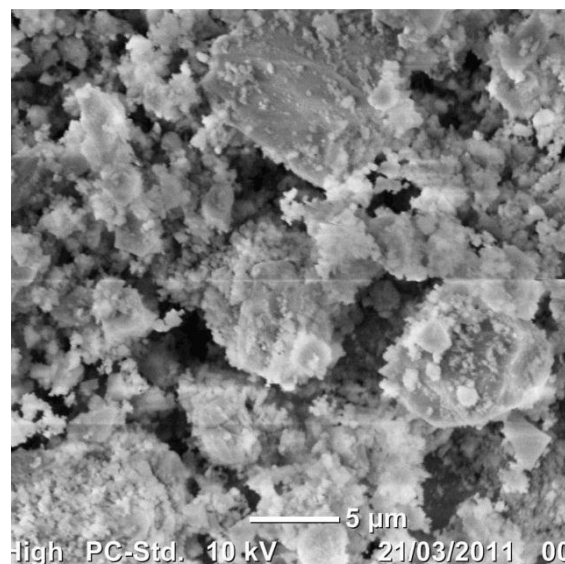
15min
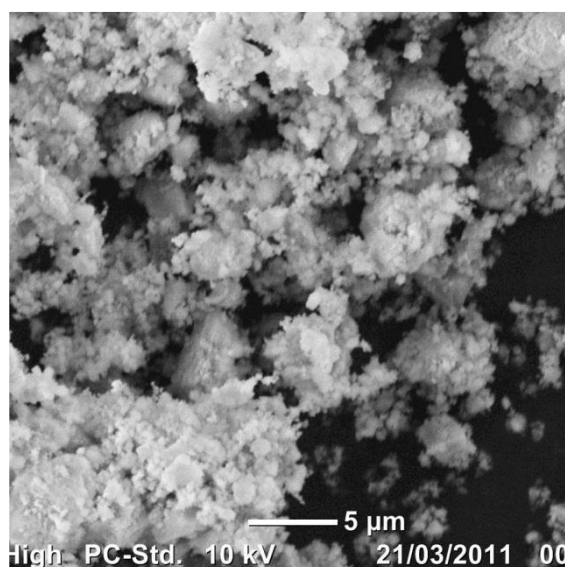
20min
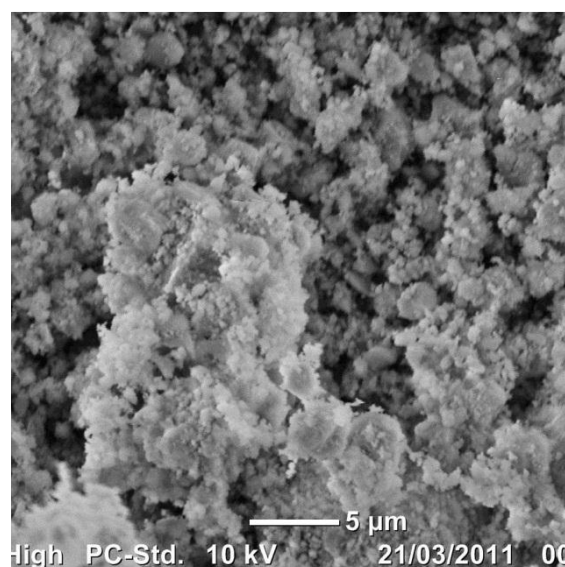
25min
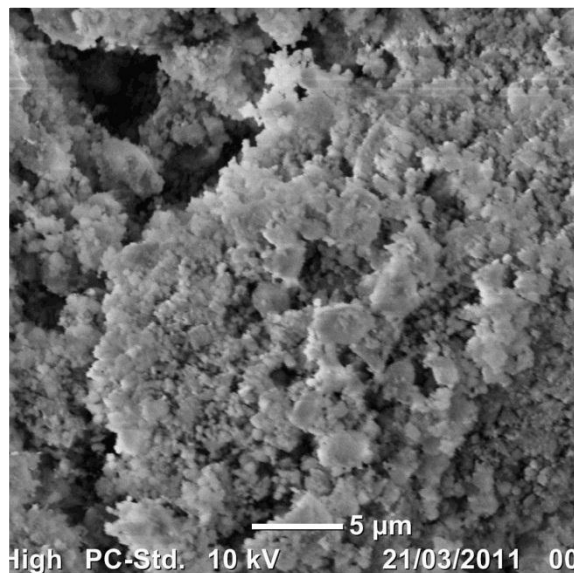
30min
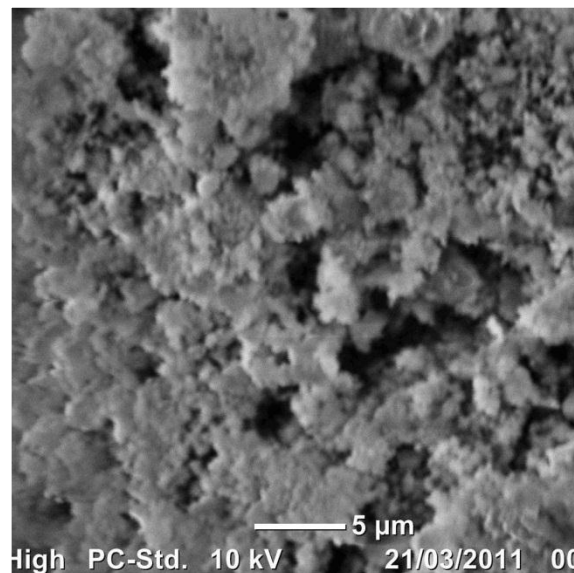
35min
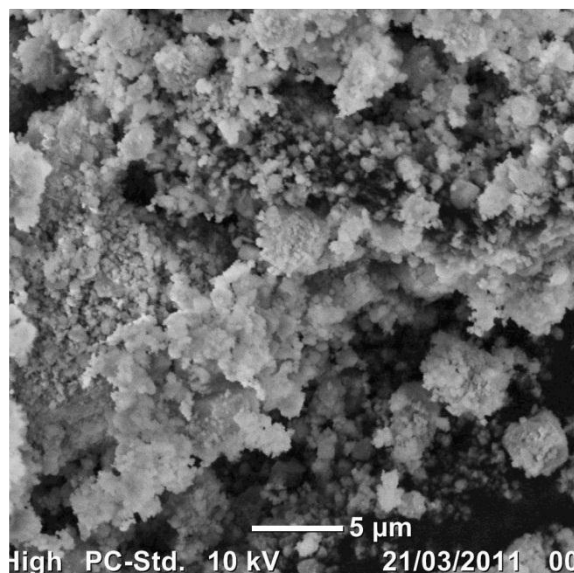
40min
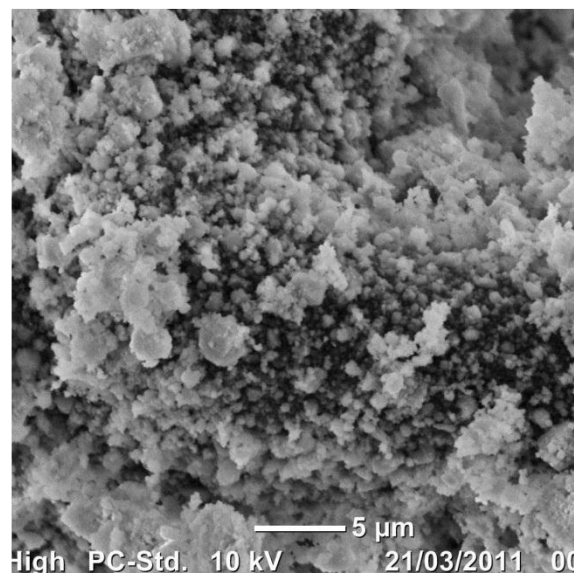
45min
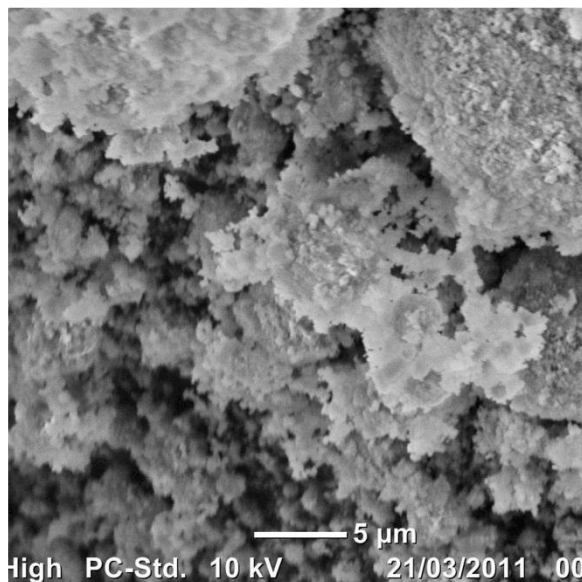
50min
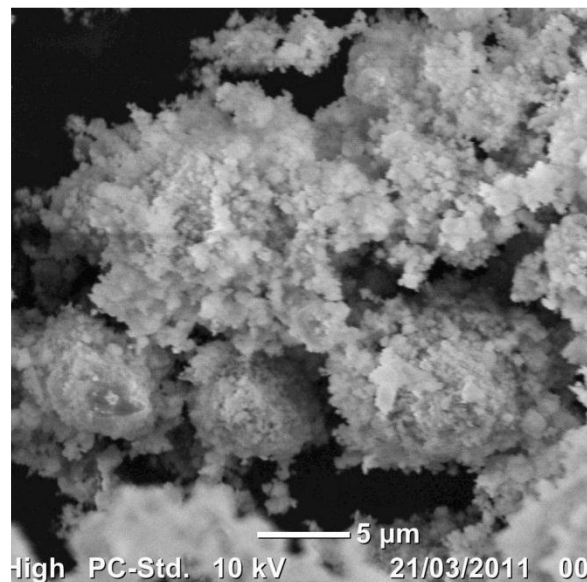
55min
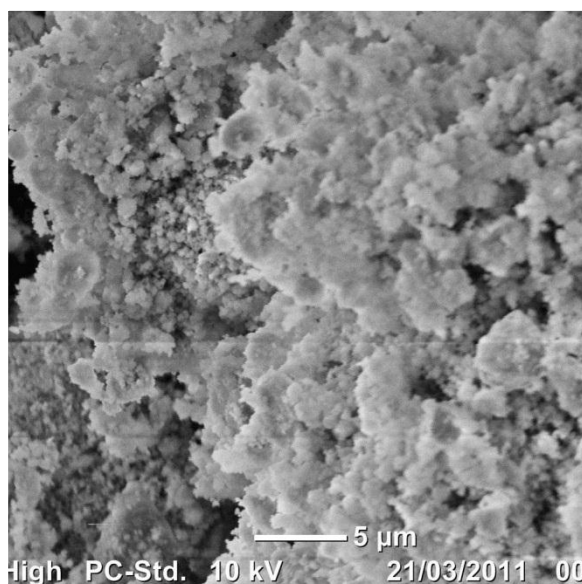
60min
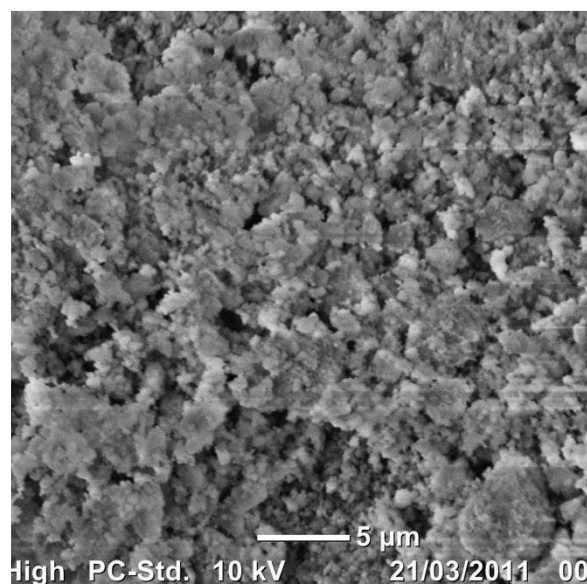
The 5 minute milling increments experiment was conducted to study the effected of ball milling on the micromorphology of quartz particles in more detail. It was thought that the decrease and increase of particle size go through a cycle before finally reaching equilibrium.

The scans suggest that this is not the case. There is a gradual decrease of particle size through the 5 minute milling increments. However, there does seem to be a sort of equilibrium occurring between 20 to 30 minute milling increments followed by some slight aggregation.

By the 50 minute milling increment the particles have a uniform look.

6.10 Limestone with Varying Water Content SEMs

6.10.1 Limestone with 0% Water

30min 0% Water
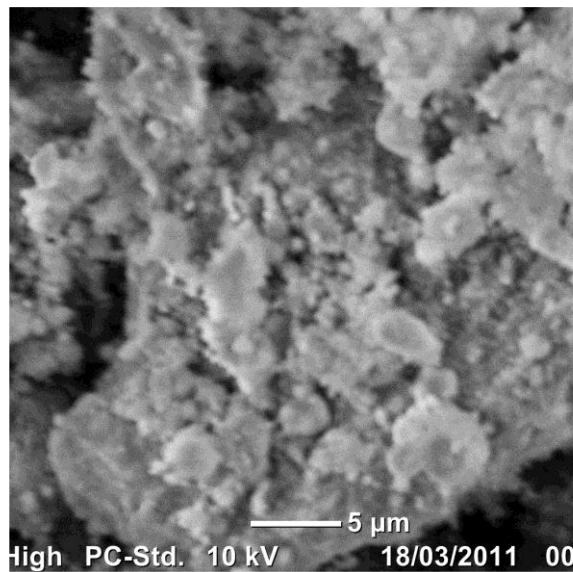
60min 0% Water
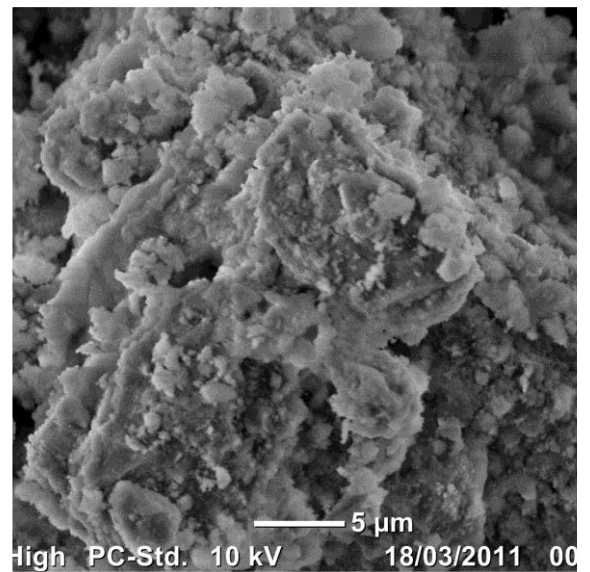
90min 0% Water
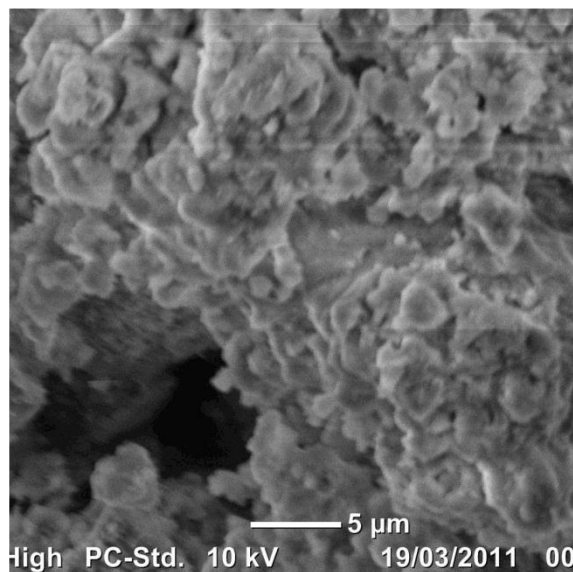
120min 0% Water
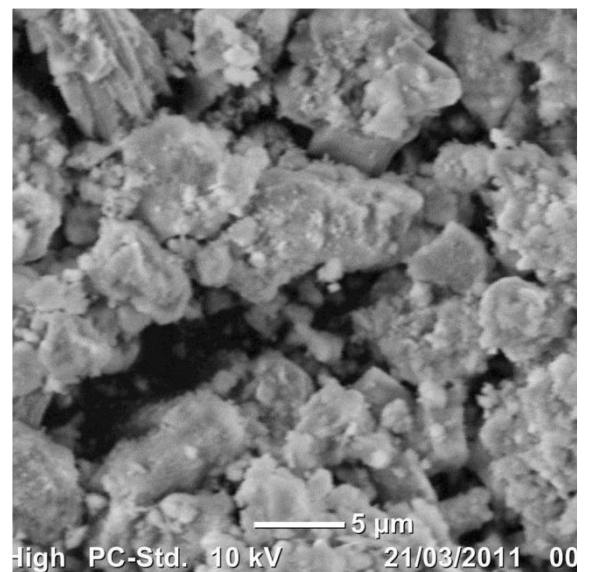
6.10.2 Limestone with 10% Water

30min 10% Water
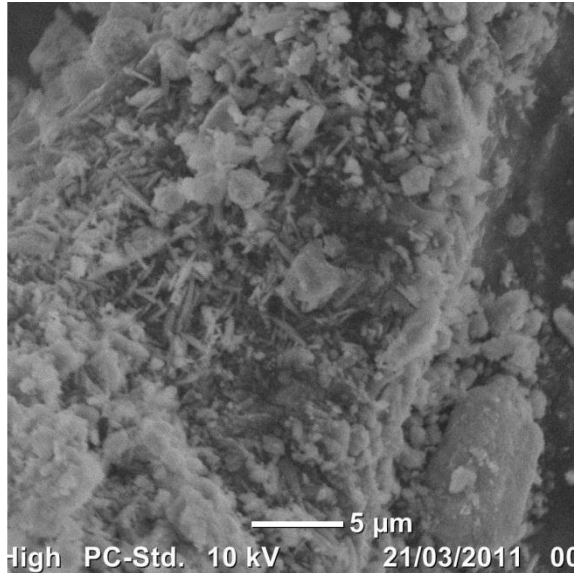
60min 10% Water
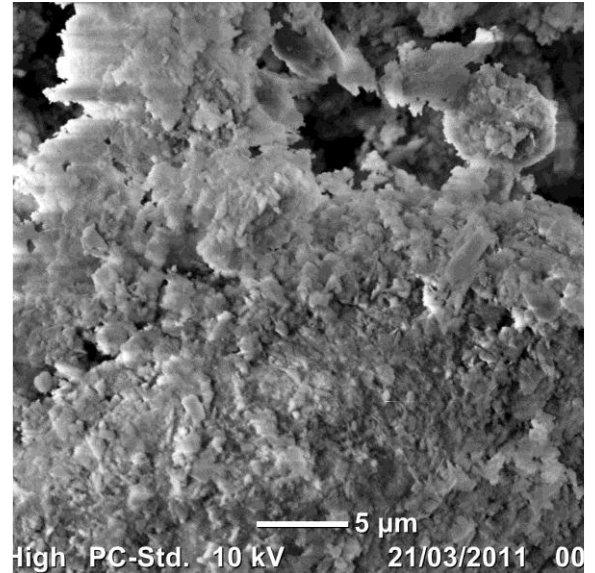
90min 10% Water
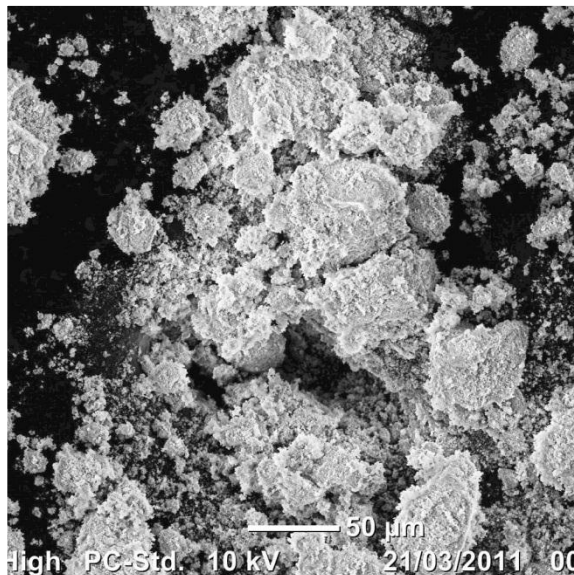
120min 10% Water
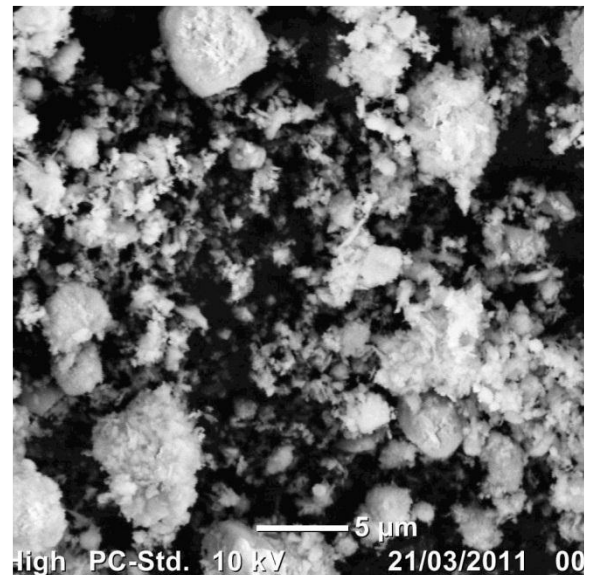
6.10.3 Limestone with 20% Water

30min 20% Water
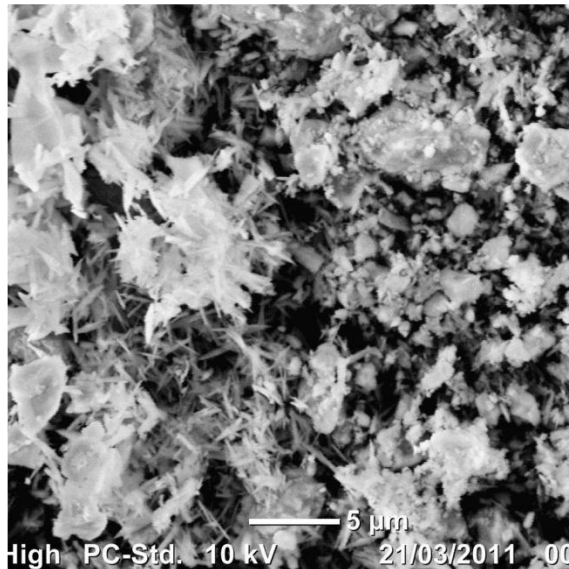
60min 20% Water
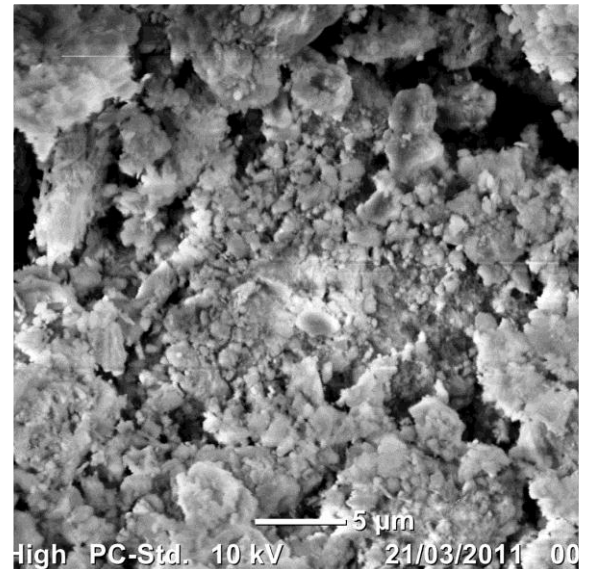
90min 20% Water
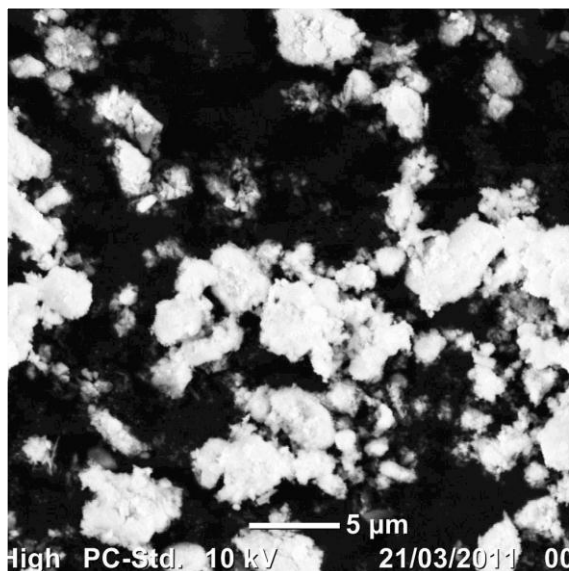
120min 20% Water
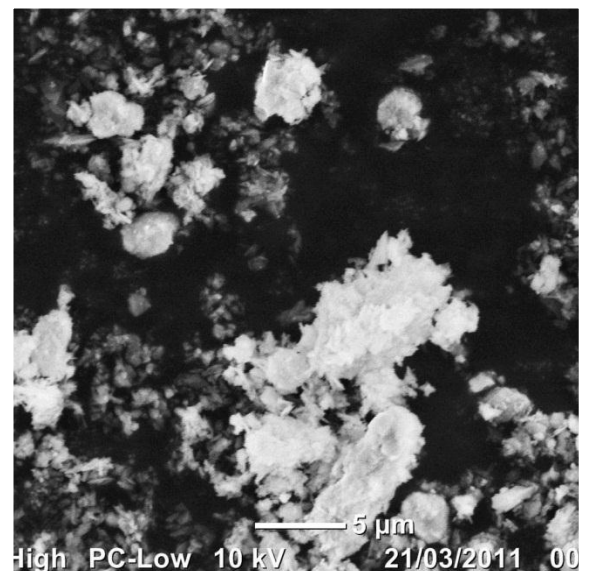
6.10.4 Discussion of Limestone SEMs

Limestone with 0% Water

Dry limestone particles had only slightly decreased in size. They did not exhibit the usual decreasing → increasing → aggregation of particle pattern of the other dry soils.

Limestone with 10% and 20% Water

Both the 10% and 20% water content limestone particles follow the Boldyrev model. The particles decrease in size during the 30 and 60 minute milling intervals, and then start to aggregate during the 90 minute milling interval. At the 120 minute milling interval, the particles decrease in size again and they are more uniformly shaped.

A micromorphology of special note is the formation of crystals mostly in the 30, 90 and 120 minute milling interval; there are some crystals present in the 60 minute mill but not as much as the other intervals.

The crystals look like aragonite; however aragonite is thermodynamically unstable at standard temperature and pressure. Furthermore the addition of water to calcium carbonate (limestone) does not produce aragonite.

Another reaction that includes water is taking place to produce these crystals. The added water must be the influencing factor as no crystals were detected in any of the 0% water milling intervals.

It is hypothesised that under the elevated temperatures of the grinding jar, calcium carbonate decomposes to give calcium oxide and carbon dioxide:

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2 \qquad \text{Equation 11}$$

At the end of the milling interval, the internal temperature of the grinding jar begins to cool down. This allows any remaining water molecules to react with the calcium oxide to produce the colourless crystal calcium hydroxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad \text{Equation 12}$$
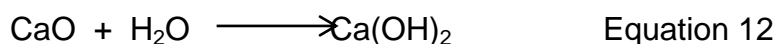
In an industrial setting, calcium oxide is usually produced by thermal decomposition of materials that contain calcium carbonate, like limestone. This is achieved by a process called calcination.

Calcination reactions take place either at or above the thermal decomposition temperature. This temperature can be defined as the temperature at which the standard Gibbs free energy of a certain calcination reaction is equal to zero. Using equation 10 as an example of a decomposition reaction, the standard Gibbs free energy can be approximated as:

$$\Delta G°r = 177100 - 158\,T\ (J/mol) \qquad \text{Equation 13 (Gilchrist 1989)}$$

For the standard free energy of reaction to equal to zero, the temperature T in equation 12 must equal 1120.89K:

$$\Delta G°r = 177100 - 158T$$
$$0 = 177100 - 158T$$
$$158T = 177100$$
$$\underline{T = 1120.89K \text{ or } 847.89°C}$$

The highest grinding jar temperature recorded was around 139°C. This of course is nowhere near the 847.89°C required to initiate calcium carbonate decomposition, however decomposition is occurring. The recorded temperature of 139°C was generated mainly by the friction between the grinding balls and the interior surface of the grinding jar. This friction-generated heat is not

involved in the decomposition of calcium carbonate. The heat that is involved in the decomposition is generated by either one or both the hot spot theory and/or the magma-plasma model. Both of these theories are capable of generating temperature that far exceeds the required 847.89°C.

It is this reasoning that leads to the hypothesis that these crystals are indeed calcium hydroxide and are being generated by the action of temperature and water.

6.11 Soil Health

The first part of these results are from the soil microbiology experiments designed to determine whether selected soil bacteria can survive the milling process and whether they would survive being introduced into freshly milled soil.

The second part of these results is from the soil fertility experiments. This experiment was designed to see whether the morphology of milled soil would be altered to such an extent that may lose its ability to sustain plant life.

6.11.1 Soil Microbiology

Two types of bacteria that are found in soils were used in the experiment. The bacteria were *Bacillus subtilis* and *Klebsiella pneumonia.* Both bacteria are involved in nitrogen fixing in soils and *Bacillus subtilis* is also used as a soil inoculant in order to free up soil nutrients for plant uptake. They were also chosen due to their contrasting nature in order to study how they both will react to the treatment. *Bacillus subtilis* is a Gram-positive obligate aerobe while *Klebsiella pneumonia* is a Gram-negative facultative anaerobe.

Bacillus subtilis was particularly chosen due to its endospore-forming ability. In its endospore form, *Bacillus subtilis* is able to tolerate extreme environmental conditions. *Bacillus subtilis* in contaminated soil would form endospores to protect themselves from the contaminants and the hypothesis was that in this form, they would also be able to tolerate the stress applied to them by the MCD treatment.

Bacterial Survival During Milling Results

B. subtilis		
Interval (min)	**Count**	**Soil Temperature (°C)**
Control	2000	16
15	500	51
30	100	89
60	0	101
90	0	119
120	0	138

K. pneumonia		
Interval (min)	**Count**	**Soil Temperature (°C)**
Control	2000	16
15	300	52
30	0	91
60	0	103
90	0	118
120	0	138

This table looks at bacteria survival during milling at 500rpm at milling intervals of 15, 30, 60, 90 and 120 minutes. More *Bacillus subtilis* bacteria survived the milling process than *Klebsiella pneumonia* did. By the 30 minute milling interval, *Klebsiella pneumonia* were completely destroyed while *Bacillus subtilis* had a plate count of about 100 colonies. This was attributed to *Bacillus subtilis'* ability to form endospores which enables it to survive temperatures around 100°C. The average temperature recorded at the end of the 30 minute milling interval

was 90°C and that temperature *Bacillus subtilis* are able to survive. There were

no surviving bacteria from 60 minute milling interval onwards.

Bacterial Survival in Freshly Milled Soil without Cooling Results

B. subtilis

Interval (min)	Count	Soil Temperature (°C)
Control	2000	16
15	2000	52
30	2000	90
60	~1500	102
90	~12	118
120	0	139

K. pneumonia

Interval (min)	Count	Soil Temperature (°C)
Control	2000	16
15	2000	51
30	0	90
60	0	99
90	0	119
120	0	139

The second table are the results of both bacterial strains being introduced into

freshly milled soil to determine whether any residual radicals, and other active

species would have a detrimental effect on the bacterial populations. This is an

important question to answer as remediation of contaminated land is usually

augmented by bioremediation. Once a contaminated site has been remediated

by chemical or thermal means, bioremediation is usually employed to ensure

any residual contaminants are degraded. Another bioremediation technique is

to use specific bacteria as a soil inoculant e.g. *Bacillus subtilis* in horticulture

and agriculture to free up soil nutrients for plant uptake, to act as antagonistic

organisms against plant pathogens and, to create a symbiotic relationship with

plant root systems.

Bacillus subtilis proved once again to be the sturdier of the two bacteria. Its

population did not decrease in either of the 15 and 30 minutes milled soil and

only experienced a small decrease in population to about 1,500 colonies from a total of 2,000 in the 60 minute milled soil. However, the *Bacillus subtilis* population greatly decreased to only 12 colonies in the soil milled for 90 minutes and no bacteria survived when introduced into the 120 minute milled soil. This data on its own is not enough to conclude that the radicals and other active species were solely responsible for the decline in bacterial populations.

Klebsiella pneumonia followed a similar pattern of declining population numbers as milling time increased. However, *Klebsiella pneumonia* was more severely affected. There was no change in population when introduced into 15 minute milled soil, but there were no surviving bacteria in the 30, 60, 90 and 120 minute milled soils.

Again, this decline in population number could not be solely attributed to the destructive effects of radicals because temperature must be taken into account.

Temperature of the soils also needed to be taken into consideration as soil temperatures reached and exceeded the lethal temperature of both *Bacillus subtilis* and *Klebsiella pneumonia* of 100°C and 71°C respectively. The decline on bacterial population could have been a result of these lethal temperatures.

Therefore another study was designed to isolate the real cause of the declining population numbers. This time the milled soil was spread over a watch glass, and placed in a freezer for 5 minutes to allow the soil to cool down.

Bacterial Survival in Freshly Milled Soil with Cooling Results

B. subtilis		
Interval (min)	**Count**	**Soil Temperature (°C)**
Control	2000	16
15	2000	31
30	2000	67
60	2000	79
90	2000	88
120	2000	101

K. pneumonia		
Interval (min)	**Count**	**Soil Temperature (°C)**
Control	2000	16
15	2000	30
30	2000	69
60	2000	80
90	500	89
120	0	100

The above table covers the results of bacterial survival in cooled milled soil. There is a dramatic difference from the uncooled milled soil. *Bacillus subtilis* suffered no population decline even though the 120 minute milled soil temperature reached 101°C. It was hypothesised that the soil temperature was further reduced upon introducing the bacteria suspended in 0.1% peptone water. The 0.1% peptone water was stored at 4°C and this was thought to have taken the temperature under the *Bacillus subtilis* lethal temperature point of 100°C.

Klebsiella pneumonia also had drastically different results, its population did not decrease up until the 90 minute milling interval. The temperature of the 60 minute milled soil was 80°C which is 9°C above the *Klebsiella pneumonia* tolerance point of 71°C (Pasteurization temperature). This discrepancy was also attributed to the cooling effect of the 0.1% peptone water used to suspend the bacteria. This would suggest that the main influencing factor of population number was due to temperature rather than radicals and other active species.

Another test designed to mimic real world mechanochemical remediation scenarios i.e. the treated soil is usually incorporated back into the site after several hours. In this scenario, both bacterial strains were each introduced into milled soils after a 12 hour waiting period.

Bacterial Survival in Milled Soil Introduced after 12 hours

B. subtilis	
Interval (min)	**Count**
Control	2000
15	2000
30	2000
60	2000
90	2000
120	2000

K. pneumonia	
Interval (min)	**Count**
Control	2000
15	2000
30	2000
60	2000
90	2000
120	2000

It is evident that after a 12 hour period, the temperature of the soil reaches ambient temperature and any radicals or active species that may or may have not affected bacterial growth would have dissipated. Both bacterial strains experienced no decrease in population numbers.

This scenario would closely resemble a real world MCD process. If it was determined that the remediation of the site had to be augmented by bioremediation, the soil would be inoculated by bacteria after a few days to weeks.

6.11.2 Discussion of Soil Microbiology Results

These results would suggest that the MCD process is detrimental to soil bacteria as depicted by the *Bacterial Survival During Milling Results.* After 60 minutes of milling, even endospore-forming bacteria would not survive.

The results also look at the feasibility of using bioremediation to augment the MCD process. The results suggest that the free radicals and active species generated during ball milling did not have an effect on the bacterial populations, but the temperature of the soils did. Bacteria that do not form endospores would not survive being inoculated in freshly remediated soil at temperatures above 70°C, while bacteria that have the ability to form endospores, would not survive being inoculated in freshly milled remediated soil at temperatures above 100°C.

This problem can be solved by simply allowing the soil to temperature to cool down before introducing any bacteria. The results from the *Bacterial Survival in Milled Soil Introduced after 12 hours* experiments showed no decrease of population numbers in either of the two bacteria species.

Augmenting the mechanochemical remediation process by bioremediation would not cause any issues after at least a 12 hour standby period.

6.11.3 Soil Fertility

The soil fertility study was conducted to determine whether the milled soil can still sustain plant life. As soils are milled, their structure, micromorphology and microorganism populations are altered.

These factors play a major role in soil health, therefore this part of the experiment was designed to study the germination rates and the number of germinating seeds of *Brassica nigra*, colloquially known as type of Mustard plants.

This plant was chosen because of it relatively fast germination rate of 3 – 10 days and also for its ability to grow well in cold, moist conditions.

The experiment was divided into three sections to study the germination speed and number as well as over health of the resulting plants in the following soils:

1. Unmilled potting mix
2. Milled potting mix
3. Mixture of milled and unmilled potting mix

The unmilled potting mix served as a control while the mixed potting mix would replicate real world conditions as areas remediated by the MCD process are usually mixed with untreated soils.

6.11.3.1 Unmilled Potting Mix

Day 3

Day 5

Day 7

Day 15

Day 25

Day 40

6.11.3.2 Milled Potting Mix

Day 3

Day 5

Day 7

Day 15

Day 25

Day 40

6.11.3.3 Milled and Unmilled Potting Mix Mixture

Day15

Day 25

Day 40

6.11.4 Germination

Unmilled Soil Seed Germination Grid

	1	2	3	4	5	6	7	8	9	10
A	X					X		X	X	X
B		X	X	X					X	
C		X						X	X	X
D	X								X	X
E									X	

X denotes successful germination

17 out of 50 seeds successfully germinated, which is a success rate of 34%.

Milled Soil Seed Germination Grid

	1	2	3	4	5	6	7	8	9	10
A	X	X				X		X		X
B	X	X						X	X	X
C			X	X	X					
D		X	X		X	X		X	X	X
E	X	X						X		X

X denotes successful germination

24 out of 50 seeds successfully germinated, which is a success rate of 48%.

Milled/Unmilled Mixed Soil Seed Germination Grid

	1	2	3	4	5	6	7	8	9	10
A				X	X	X	X	X		
B	X			X	X	X	X	X		X
C			X			X			X	X
D		X	X	X			X		X	
E		X	X	X		X				

X denotes successful germination

25 out of 50 seeds successfully germinated, which is a success rate of 50%.

6.11.5 Discussion of Soil Health Results

All of the soils managed to sustain the growth of the Mustard plants but slightly differing germination and growth rates. The germination success rate of the unmilled soil was the lowest at 34%, followed by 48% in the milled soil and 50% in the milled/unmilled soil mixture.

The milled soil was not able to retain much of the water due to the soil's altered micromorphology. The milled soil was not agitated to allow for aggregation and the soil lost approximately 110ml from a total of 150ml. Therefore, the milled soil had a retention capacity of 27%. The unmilled and mixed soils only lost approximately 20ml each, giving them a retention capacity of 80%. It is important to note that during preparing the mixed soil sample, the soils were agitated as a result of the mixing process. This agitation along with the introduction of the aggregated unmilled soil allowed for a more healthy soil structure to form. The process of mixing milled and unmilled soils would occur in

a real world scenario; this part of the study reflects this scenario and allows for useful results which can be applied to a real remediation project.

All the plants reached maturity, however differences in leaf size and the lengths of the stems were apparent. The plants growing in the milled soil had smaller leaves and shorter stems than the other two plants.

The colour of the leaves of the plants in the milled soil was also different, some exhibited a yellow colour while other leaves were withering, but the majority of the leaves were bright green and healthy looking. The other two plants had much larger leaves and grow taller overall and none exhibited yellow leaves. They also grew much denser than the plants in the milled soil. In a real world contaminated land remediation scenario, the remediated soil that has been put through the MCD process is mixed with unmilled uncontaminated soil and then put back into the site. The soil is then tilled to ensure homogeneity.

The soil fertility experiment of the milled/unmilled mixture was carried out to mimic this real world scenario to determine how the soil performs in an agricultural context. The results suggest that the soil would be fertile and would be able to sustain plant life.

Chapter 7 – Conclusion & Recommendations

7.1 Conclusion

The objectives of this research were fourfold:

1. To study the behaviour and destruction rates of organic molecules in a variety of soils to investigate some of the soil classes as depicted in the soil texture triangle.

2. To determine the way water decreases the destruction rates of organic molecules in wet soils and whether completely drying the soil or merely reducing the water content to a certain concentration was required to achieve acceptable destruction rates.

3. To determine the effect of organic matter on the destruction rates in a variety of soil types.

4. To determine what effect ball milling has on the soils' micromorphology and on microorganisms.

All the soils generally allowed for the destruction of naphthalene, chloronaphthalene and diesel. However, some soils yielded greater destruction rates than others. The soils are listed below from highest to lowest destruction rate achieved:

1. Quartz   3. Limestone   5. Greywacke   7. Terracotta clay

2. Scoria   4. Subsoil   6. china clay

By the end of the milling cycle, all the soils except for terracotta clay had reached significant naphthalene destruction rates i.e. the amounts of the

remaining naphthalene ranged had dropped to approximately 0.15 of the original concentration.

During the chloronaphthalene tests, the destruction of chloronaphthalene for both quartz and scoria at the end of the milling cycle was close to 100%; however for limestone and sub soil, destruction rates were 74% and 75% respectively.

The diesel tests followed the pattern of the naphthalene and chloronaphthalene tests. There was a steady decrease in diesel concentrations as milling time increased. By the end of the milling cycle, quartz and scoria had destruction rates of 95% and 94% respectively. Limestone and subsoil did not perform as well as quartz and scoria; they had destruction rates of 81% and 60% respectively.

Using cellulose as a model for organic material that would naturally occur in soils, it was found that the destruction of naphthalene was hindered in all the soil samples. As the cellulose concentration increased, the destruction rate decreased. The limestone destruction rates with 0, 2, 5 and 10% cellulose concentration were 98, 84, 70 and 58% respectively by the end of the standard milling cycle. The quartz destruction rates with 0, 2, 5 and 10% cellulose concentration were 100, 100, 97 and 98% respectively by the end of the milling cycle and the subsoil destruction rates with 0, 2, 5 and 10% cellulose concentration were 98, 95, 95 and 96% respectively by the end of the milling cycle.

The clay drying tests for both terracotta and china clay generally yielded similar results. As the drying temperature was increased more bound water was lost from the clay which resulted in a greater destruction rate of naphthalene.

There was however some differences; because terracotta clay had a much higher initial water content than china clay. This increased water content significantly hampered the destruction of naphthalene. The naphthalene destruction rate increased by 26% from the undried sample to the sample dried at 800°C by the final milling interval. On the other hand, china clay destruction rate only increased by 7% from the undried sample to the sample dried at 800°C by the final milling interval.

The moisture trials were conducted on quartz, scoria, limestone and subsoil. Naphthalene was the pollutant analogue. The quartz moisture trial yielded three distinct groups:

1. The 0% water sample
2. The 60% water sample
3. The remaining samples (1, 2, 3, 4, 5, 10, 20 and 40% water concentrations).

Quartz had the highest destruction rate during each milling interval when it was completely dry (83, 86, 98, 99 and 99%) and had the lowest destruction rate when 60% by weight of water was added (54, 66, 67, 70 and 71%). The remainder of the samples all had destructions rates between the 0% and 60%. They roughly followed similar degradation of naphthalene, and by the final milling interval had an average destruction rate of 94%. This decrease in destruction rate is attributed to the radical scavenging effects water has as demonstrated by the water induced intermediates in section 5.3.

The other soils in the moisture trials exhibited the same trend as the quartz moisture trial, their destruction rates decreased as water concentrations increased.

The final objective was to study the effect of ball milling on the health of the soil. The first part of the soil health study looked at the soil microbiology. It had been assumed that residual free radicals in milled soil would kill microorganisms. Both the *Klebsiella pneumonia* and *Bacillus subtilis* did not survive past the 60 minute milling interval, but they were able to survive being inoculated into milled soil that had been given time (12 hours) to cool down, these results suggest that the temperature of the soil is more important than the free radical content but more importantly show that the re-introduction of microorganisms can be done reasonably safely. This would also be important where milling and bio-remediation are combined. The second soil study looked at the soil's structure *via* scanning electron microscopy and by planting mustard seeds. Most of the soils exhibited a trend of decreasing particle sizes by the 30 minute milling interval, followed by an increase in particle size (aggregation) by the 60 and 90 minute milling interval and then would reach a point of equilibrium where the particle sizes would not greatly fluctuate. The mustard plant growth experiment revealed that milled soils were capable of sustaining plant life. The mustard seeds had a germination rate of 34% and yielded healthy mature plants in the unmilled (control) soil. The germination rate of seeds planted in the milled soil was 48% but the plants were not as vigorous as the control however, the water retention was also far less than the control and mixed soils. The milled soil had a retention capacity of only 27% while the control and mixed soil had a retention capacity of 80% which will influence plant growth.

These results have shown that mechanochemical remediation of soils contaminated by organic pollutants is a successful method. Water does hinder destruction rates, but so long as these are not mechanical issues with the mill operation, such as severe ball coating from the wet matrix, drying the soil to a

water concentration below 20% could yield acceptable destruction rates. Furthermore, if the milling cycle is extended to 3 hours the destruction of any organic pollutant would probably be close to complete. The same applies to soils rich in organic material as the cellulose experiment demonstrated that it would initial reduce destruction rates, but towards the end of the milling cycle the destruction rates of naphthalene were high enough, and again, extending the milling cycle to 3 hours would completely destroy all pollutants.

Ball milling does affect the soils' immediate utility for growing plants, but mixing milled soil with unmilled soil would doubtless solve most of these problems and soil bacteria can be safely introduced to enhance the soils' fertility and/or augment the remedial work via bioremediation once the soil reaches ambient temperature.

6.2 Further Studies and Recommendations

1. Look for intermediates produced during milling soils with high organic matter concentrations. The results of this experiment and literature lead to a hypothesis that cellulose was sequestering the naphthalene, but a detailed study into the intermediates in the 30 minute milling sample would shed some light on the mechanochemistry behind the sequestration and whether the naphthalene molecules were indeed being sequestered.

2. To further study the intermediates produces during the milling cycles, a TOC analyser should be used to in conjunction with a GC-MS to allow for a more rigorous analysis.

3. Increasing the milling cycle to 3 hours or more to find the exact milling time required to fully degrade an organic pollutant in soils with high organic and water concentrations.

4. Design a study to investigate whether the heat generated during the milling process would be sufficient to dry wet soils. This would negate the need to dry very wet soil beforehand. A study into milling time and temperature would also be needed to ensure that the soils is being subjected to a sustained elevated temperature for long enough to promote drying.

5. A study should look into the financial feasibility of employing extended milling times over the addition of a drying process. The extended milling time may prove to be effective in initially drying the soils and then degrading any pollutants, but this extended milling period may cost a lot more money and time than using specifically designed soil dryers.

6. Further study should be made on the red colouration that is developing in extractions of soils milled at the 90 and 120 minute milling intervals as the results obtained during this study were inconclusive.

7. As mentioned in the methodology section, the ultrasonic bath was used to augment the extraction process. Halfway through the study, it was thought that the process of sonification might have been contributing to the destruction of naphthalene. Therefore, ten identical samples (5000ppm of naphthalene in 50g of quartz) were milled under exact milling condition (30 minutes each). All the samples were extracted by the same extraction processed described in the methodology section except five of the samples were not agitated in the ultrasonic bath while the remaining fiver were. After analysing the sample, they all yielded very

similar results. It seems that the sonification process did not contribute to the extraction process let alone destroy naphthalene. The use of the ultrasonic bath was continued for the sake of consistency, as all the previous experiments were sonified. It therefore recommended that any future experiments need not use the sonification bath during extraction.

8. The soil fertility test was carried only as a preliminary test to quickly investigate whether milled soils would be able to sustain plant life. Therefore, a more rigorous analysis did not seem necessary. It would be recommended that any future studies into soil fertility employ a more rigorous methodology. Suggestions would be to treat each row in the seed grid as a replicate and calculate the germination rate for each row. This would allow for statistical analysis e.g. t-test to be used and scientifically demonstrate that the control versus milled treatments were significantly different. Likewise, the plant morphology analysis can be enhanced by a more quantitative approach i.e. measure the actual leaf size and stem length and also use statistical analysis.

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