

## MechanoChemical Destruction Treatability Study

PCB Contaminated Soils  
Parcel E Shoreline  
Hunters Point Shipyard  
San Francisco, California  
United States of America

## Final Report

Contract Number N68711-01-D-6011  
July 2006





## **FINAL REPORT**

# **MECHANOCHEMICAL DESTRUCTION (MCD™) PCBS TREATABILITY STUDY**

***Parcel E Shoreline  
Hunters Point Shipyard  
San Francisco, California  
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***Environmental Remedial Action  
Contract Number N68711-01-D-6011  
Contract Task Order 0001  
Document Control Number NAV001-114-H  
Revision 2 (final)***

***July 2006***

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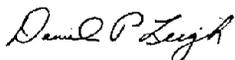
## FINAL REPORT

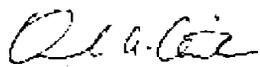
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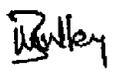
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## Acronyms and Abbreviations

%	percent
°C	degree(s) Celsius
µg/l	micrograms per liter
µg/kg	micrograms per kilogram
CO <sub>2</sub>	carbon dioxide
CTO	Contract Task Order
DDD	Dichloro-Diphenyl-Dichloroethane
DDT	Dichloro-Diphenyl-Trichloroethane
DE	Destruction Efficiency
EDL	Environmental Decontamination Ltd
EMAC	Environmental Multiple Award Contract
EPA	US Environmental Protection Agency
HCB	hexachlorobenzene
HPS	Hunters Point Shipyard
mg/l	milligrams per liter
mg/kg	milligrams per kilogram
MC	mechanochemical
MCD™	Mechanochemical Destruction (Trademark of EDL)
MSDS	material safety data sheet
Navy	US Department of the Navy
O <sub>2</sub>	oxygen
OCPs	Organochlorine Pesticides
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCP	pentachlorophenol
PIMS	Phosphate Induced Metal Stabilization
RI	Remedial Investigation
RU	Remedial Unit
SAC	Soil Acceptance Criteria
STLC	Soluble Threshold Limit Concentration
SVOC	semi-volatile organic compound
TCLP	Toxicity Characteristic Leaching Procedure
TOC	Total organic carbon
TPH-d	total petroleum hydrocarbons as diesel
TPH-mo	total petroleum hydrocarbons as motor oil
TS	Treatability Study
USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound



## 1.0 Executive Summary

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At the request of the US Department of the Navy (Navy), Shaw Environmental (Shaw) and Environmental Decontamination Ltd (EDL) were commissioned to conduct a MechanoChemical Destruction (MCD™) Treatability Study, on site at Hunters Point Shipyard (HPS), San Francisco. The Treatability Study (TS), conducted in May 2006, evaluated the potential for the MCD™ Series III technology to remediate soil in HPS PCB Hotspot Stockpiles 5, 6 and 7. The TS also evaluated the post MCD™ stabilization of metals using phosphate induced stabilization. Three 50 lb representative soil samples were taken from each stockpile for use in the TS.

Primary contaminants of concern in PCB Hotspot Stockpiles 5, 6 and 7 are Arochlor 1260 PCBs and Lead (Pb), at up to 170,000 µg/kg and 2,100 mg/kg respectively. Secondary contaminants include diesel and motor oil hydrocarbons, organochlorine pesticides (OCPs) and a wide range of metals. Each PCB Hotspot Stockpile contains approximately 3,000 ton of contaminated soil. The Soil Acceptance Criteria (SAC) for the TS, as determined by the Navy, are 1,000 µg/kg PCBs and 5 mg/l Toxicity Characteristic Leaching Procedure (TCLP) Pb. These strict SAC ensure a very high standard of remediation, allowing reinstatement of remediated soil on site at any depth.

The MCD™ technology successfully achieved remediation to below the PCB SAC (<1,000 µg/kg) in all samples processed under standard MCD reactor operating conditions. PCB concentration in several MCD treated samples was reduced to non-detect (<15 µg/kg) at destruction efficiencies >99.95%.

Based on extensive laboratory research by EDL and other researchers, PCBs are converted to a high molecular weight amorphous carbon product and inorganic chloride during MCD treatment. Based on the total organic carbon results from the TS, and published literature, the carbon may then go on to form CO<sub>2</sub> and inorganic carbonates. The inorganic chloride already in the soil and released from the PCBs is progressively bound to the mineral compounds in the soil matrix and is not extractable as soluble chloride.

Arochlors 1248 and 1254 were detected in similar concentrations to Arochlor 1260 in several MCD™ treated samples. Detection of small amounts (<1% of original compound concentration) of dechlorination products such as these are often observed during MC treatment of organochlorines, and their presence is confirmation that mechanochemical destruction reactions have occurred. Having said that, further MC treatment results in the destruction of all organic



breakdown products, as observed in several MCD treated samples where all Arochlors were below the detection limit.

MCD™ remediation of OCPs (DDT and dieldrin) in TS soil samples was also achieved with concentrations reduced to below the detection limit (<17 µg/kg). The initial concentrations were low (<10 mg/kg) and destruction efficiencies >99.2% are restricted by the detection limit.

Mass balances on carbon and chloride are difficult for several reasons. For carbon, a variety of mechanochemical reactions can occur, including destruction of organics, formation of CO<sub>2</sub>, carbonates and carbides, and grafting of carbon compounds on to inorganic mineral phases. Hence more comprehensive analytical techniques than total organic carbon are needed to account for all carbon species. For chloride, a simple soluble chloride test is of limited value due to the binding of inorganic chloride by the inorganic soil matrix. The variable background inorganic chloride concentrations, the low initial PCB concentrations and the complexity of treating real contaminated soils at pilot scale are other significant issues. As with carbon, more comprehensive analytical techniques are needed account for all chloride species.

Stabilization of metals occurred during MCD™ treatment resulting in a mean TCLP result for Pb of 0.55 mg/l, comfortably below the SAC of 5 mg/l. This positive result is attributed to mechanochemical stabilization reactions (interaction of soil minerals and metals) and the breakdown of EDL reagents to release common stabilizing ions in the MCD™ reactor. The positive result above made the phosphate induced stabilization step using Apatite II™ largely redundant. The mean TCLP Pb result for the stabilized samples was slightly lower at 0.16 mg/l. The TCLP results for other metals were also very low and well below SAC levels for each. In California however the Soluble Threshold Limit Concentration (STLC) is also used to measure leaching of metals. The STLC results were not as conclusive with several samples exceeding the SAC of 5 mg/l for Pb and 5 mg/l for Cr. The minimal addition of water during stabilization treatment may also have a detrimental affect on results.

The TS demonstrates the potential for the use of a full scale MCD™ plant at HPS for the remediation of PCBs. Remediation to below the SAC (1,000 µg/kg PCBs) can be achieved. The TS results have naturally been interpreted based on independent published research and unpublished research performed by EDL on the mechanochemical destruction of organic compounds. Based on this knowledge and the TS results, the mechanochemical destruction of PCBs in HPS soil does occur. The difficulty in closing the carbon and chloride mass balances,



and the lack of gas sampling and analysis data from the TS, means that volatilization of PCBs during MCD™ treatment cannot be totally discounted. Intelligent design of experiments and the use of exotic analysis techniques should enable closing of mass balances. Gas sampling at the inlet and outlet of the MCD™ reactor is recommended during subsequent application of the MCD™ technology at pilot or full scale to ensure release of volatilized PCBs does not occur.

Stabilization of metals to below the SAC is possible using USEPA endorsed TCLP analysis. If STLC analysis is used then modification of the stabilization treatment will be required. Stabilization technologies in common use for a number of years have proven successful at meeting the SAC via STLC analysis and hence stabilization to this standard using similar methods should be achievable.

Mathematical modeling based on the TS results indicates that the throughput of a full scale MCD™ plant utilizing 2 full scale MCD™ reactors will be approximately 6 t/hr. Assuming plant availability is 40 hrs/wk, it will take approximately 40 weeks to remediate the 10,000 ton of soil in the PCB Hotspot stockpiles. Additional MCD™ reactors and extended operating hours will reduce the duration of the remediation project.



## 2.0. Introduction

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This MechanoChemical Destruction (MCD™) Treatability Study Report has been prepared by Environmental Decontamination Ltd (EDL) and Shaw Environmental, Inc. (Shaw) for the U.S. Department of the Navy (Navy), Naval Facilities Engineering Command, Southwest Division, under Contract Task Order (CTO) 0001 and Contract Number N68711-01-D-6011. The Treatability Study (TS) was performed by EDL and Shaw following the plan detailed in *Internal Draft Work Plan, MechanoChemical Destruction Treatability Study, HPS PCB Hotspot Stockpiles 5, 6, 7, Hunters Point Shipyard, San Francisco, California* (herein referred to as the Work Plan) (Shaw, 2006). The TS was conducted in Building 414, Hunters Point Shipyard (HPS), San Francisco, in May 2006.

### 2.1. Site Description and Background

HPS is located in the City and County of San Francisco, California. PCB contaminated soil has been excavated and stored in PCB Hotspot Stockpiles 5, 6 and 7 awaiting remediation or suitable disposal off site.

HPS was utilized as a shipyard since the late 19<sup>th</sup> century. Beginning in the 1940s, the Navy operated HPS as a ship repair and maintenance facility until 1974. From 1976 to 1986, the Navy leased HPS to Triple A Machine Shop, a private ship repair company. In 1989, due to the presence of hazardous materials from past Navy and Triple A operations, HPS was placed on the National Priorities List, pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act, as amended by the Superfund Amendments and Reauthorization Act of 1986. In 1991, HPS was selected for closure pursuant to the terms of the Defense Base Closure and Realignment Act of 1990 (Public Law 101-510). Closure of HPS includes conducting environmental remediation activities and transfer of the property to the City of San Francisco for future non-defense reuse.



## 2.2. Objectives

The goal of the TS was to remediate nine PCB Hotspot soil samples contaminated with PCBs and heavy metals to below the target SAC of 1,000 µg/kg PCBs and 5 mg/l Pb (TCLP). The TS was designed to provide a sound technical basis for comparing this technology with other PCB and heavy metal soil treatment alternatives. The following objectives were established to meet this goal:

- Provide data sufficient to evaluate the effectiveness, implementability, and cost of the technology as applied to a full-scale remediation. The U.S. Environmental Protection Agency (EPA) document entitled, *Guidance for Conducting Remedial Investigations and Feasibility Studies under the CERCLA* (USEPA, 1988), was used in determining the data requirements necessary to support these objectives within the study.
- Obtain baseline concentrations for PCBs and metals in HPS soil.
- Obtain data to evaluate the viability and effectiveness of MCD™ treatment technology for destroying PCBs in HPS soil.
- Obtain data to evaluate the viability and effectiveness of phosphate induced metal stabilization (PIMS) using Apatite II™ in stabilizing metal contaminants in HPS soil.
- Continue to refine best management practices in this new technology.

## 2.3. Scope of Work

The scope of work for the TS is detailed in the Work Plan (Shaw, 2006). In summary, soil samples were dried in an incubator to reduce the moisture content to <2%. Samples 01, 05, & 07 were manually screened to generate a >5 mm particle size fraction for PCB analysis. Soil samples were MCD™ treated individually for a total of 45 minutes with analytical samples taken at 15, 30 and 45 minutes. Following MCD™ treatment Soil Samples were metal stabilized using Apatite II™ to induce phosphate stabilization.



### 3.0. *MechanoChemical Destruction of PCBs and Stabilization of Metals*

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This section provides background and technical information on the MCD™ treatment and metal stabilization processes.

#### 3.1 *MechanoChemical Destruction Treatment*

MC destruction of toxic organic compounds was first reported by researchers at University of Western Australia (Rowlands et al., 1994; Donecker et al., 1994; Hall et al., 1996). DDT and other organic compounds were destroyed by MC treatment in the presence of calcium oxide to a carbon residue and inorganic chloride. A detailed investigation into the mechanochemical destruction of DDT in calcium oxide was conducted by Hart (2000). Researchers in Japan have continued to investigate the MC destruction of organic compounds in calcium oxide (Zhang et al., 2001, 2002; Ikoma et al., 2001; Tanaka et al., 2003a, 2003b, 2004).

MC destruction of organic compounds also occurs in alumina, quartz and other silicate materials. The principal mechanism is high energy impacts in the MC treatment result in the cleavage of Si-O bonds to form free radicals at E' centers ( $\equiv\text{Si}^{\cdot}$ ) and non-bridging oxygen hole centers (NBOHC) ( $\equiv\text{Si}-\text{O}^{\cdot}$ ) (Heineke, 1984; Steineke et al., 1987; Hasegawa et al., 1995). There is a relationship between the fracture strength of materials and the rate of destruction yet, even clays, which are mechanically very weak, show these free radical forming fractures (Frost et al., 2002).

These radicals react with organic molecules breaking them down into a carbon/silicate matrix and, in the case of organochlorines, inorganic chloride (Field et al., 1997; Kaupp et al., 2002).

Our research is consistent with a primarily free radical mechanism for the destructive process. However, there is also evidence from our studies and those of others that other MC processes contribute to the destruction of organic compounds, including the formation of tribo-plasmas, emission of free electrons and photons, and the formation of molecules in highly excited states (Heineke, 1984). Heineke (1984) concludes that MC reactions do not occur via simple uniform mechanisms.

Field et al. (1997) investigated the MC reaction of various aromatic hydrocarbons (naphthalene, anthracene, biphenyl and phenanthrene) with alumina and silica. After 24 hours of grinding, these



compounds were converted largely to graphitic carbon as identified by powder X-Ray crystallography. At intermediate stages of MC treatment, a number of breakdown products were detected in significant yields. Destruction of the above compounds was considerably faster in silica than in alumina. A mass balance of the carbon in the aromatic compound prior to MC treatment and the graphitic carbon after MC treatment was very good.

Tetrabutyltin, o-dichlorobenzene, dioxins and Nitrofen have been mineralized into a graphitic substance through MC treatment in the presence of quartz (Kaupp et al., 2002, 2003). E' centre and NBOHC radicals, and other highly reactive species, on the freshly cleaved surfaces of the quartz are responsible for the destruction of organic compounds. When glass is used as the inorganic matrix a closed loop process is possible where after MC treatment the micron particle size glass can be melted and the carbon combusted. The glass can then be crushed and used for further destruction of organics (Kaupp et al., 2003). A wide range of other MC reactions are also possible (Kaupp, 2005).

The research referred to above focuses mainly on the destruction of pure organic compounds and is limited to laboratory scale applications. EDL on the other hand has focused on the MC remediation of contaminated soils and has proven full scale experience with the MCD™ plant remediating the Mapua site. EDL has worked extensively with the Foundation for Research Science & Technology, the New Zealand Ministry for the Environment and Auckland University of Technology (AUT) throughout the R&D program. This R&D led directly to the full scale trial of the MCD™ technology at Mapua, New Zealand's worst pesticide contaminated site. This site was contaminated with DDT and dieldrin at over 3,000 mg/kg. Following the successful proof of performance trial in April 2004, EDL was awarded the contract to remediate the Mapua site, and is presently operating the only full scale MechanoChemical Destruction (MCD™) plant in the world. Remediation of this 5 hectare site is scheduled to be complete late 2006.

Extensive laboratory and pilot research has been conducted on a wide range of organic contaminants in a number of model and real soils. While quartz sand has been the principal synthetic soil for most of the research work, real soils used have been various clay and limestone rich samples, ground basalt and very organic rich topsoil. Contaminated Mapua soil is a typical complex mixture of feldspars, quartzites, clays, carbonates and other organic and inorganic matter. Successful MC destruction of a number of different organic compounds has been accomplished in several soil types using a variety of milling devices. This suggests that MC



destruction of organic compounds can be developed into a robust and versatile chemical process (EDL, unpublished research)<sup>1</sup>.

Contaminants successfully destroyed include pentachlorophenol, naphthol, hexachlorobenzene, naphthalene, pyrene and other PAHs, PCBs, chloronaphthalene, bromo and chlorobenzene, various petroleum hydrocarbons (including diesel) , 2,4-D, 2,4,5-T, organophosphate and carbamate pesticides. MC destruction shows pseudo-first order kinetics for all compounds and destruction efficiencies >99.99% have been achieved (EDL, unpublished research).

The final organic products detected for the MC treatment of all organic compounds has been shown by Raman spectroscopy and other analysis to be amorphous carbon (Tanaka et al., 2003a; Field et al., 1997; Kaupp et al., 2002; EDL, unpublished research).

The chlorine produced from organochlorine compounds, is converted to chloride (probably initially as a chlorine radical which picks up a free electron from the fracture surface). Some of the chloride can be extracted from samples with water but the majority is bound into the inorganic matrix (EDL, unpublished research). An x-ray photoelectron spectroscopy (XPS) examination of a very high concentration naphthalene (10,000 mg/kg) and sodium chloride (20,000 mg/kg) sample after MC treatment showed no evidence of carbon chlorine bonds despite the marked reduction in soluble chloride concentration (<50%). The reduction in soluble chloride concentration (>6,000 mg/kg or >0.6%) is high enough to allow XPS detection of C-Cl bonds if significant (detection limit of XPS 0.1%) (EDL, unpublished research). Halogen cross-over studies with bromo and chloro benzene and naphthalenes also support this (EDL, unpublished research).

In the laboratory, headspace studies have shown that some water, carbon dioxide, carbon monoxide, methane and possibly hydrogen are produced during milling (EDL, unpublished research).

Intermediate breakdown products resulting from dechlorination and cleavage of alkyl/aromatic C-C bonds are observed with some starting compounds (EDL, unpublished research). In the presence of moisture -OH addition has been observed and with atmospheric oxygen (O<sub>2</sub>) present trace amounts of oxygenated species are detected. In the absence of O<sub>2</sub> no oxygenated organic

<sup>1</sup> EDL has performed hundreds of laboratory, pilot and full scale trials during R&D of the MCD technology. Much of this was done by Tristan Bellingham during the course of his doctorate, supported by staff and students at Auckland University of Technology (New Zealand). This research is presently being prepared for publication in international environmental and chemistry journals and the research results (in draft form) are available from EDL on request.



compounds are formed (EDL, unpublished research). Although MC polymerization of several organic monomers has been achieved (Hasegawa et al., 2001, 2002) these are much milder conditions and we have only observed progressive destruction in our studies. The maximum concentration of intermediates is generally <1% of the starting organic compound concentration and all intermediates are subsequently destroyed as MC treatment continues (EDL, unpublished research). The MC destruction rate of different organic compounds is dependent on chemical structure, primarily that of the carbon skeleton. For the compounds we have studied, structures with lower ionization energies such as aromatics (for example PAHs) are rapidly destroyed. Molecules with higher ionization energies and more stable free radicals are slower (for example linear hydrocarbons) (EDL, unpublished research).

Initially, bench top, pilot and full-scale work was carried out using conventional vibratory and planetary milling devices. EDL research identified significant shortcomings in the vibratory ball mill mechanics with respect to initiating MC reactions, and set about developing a purpose built mechanical reactor that would meet the challenges of effective, eco-efficient MC destruction. This optimized reactor design, designated Series III, is presently in full scale operation at Mapua. A pilot Series III MCD™ reactor has been fabricated for use in treatability studies such as this. The operational principles of the pilot and full scale Series III MCD™ reactors are identical and macro kinetic modeling can be used to predict full scale performance based on pilot scale TS results.

EDL has filed several patents (New Zealand Patent Numbers 545960, 545961) to protect its research and development investment in the MCD™ technology. The company has filed patent protection essentially in the areas of multi-tube MCD™ reactor design, and the simultaneous full-scale operation of MC destruction of organic pesticides in conjunction with heavy metal stabilization.

### ***3.2 Post MCD™ Metals Stabilization***

Phosphate induced metals stabilization (PIMS) is established as a proven method of metal stabilization (USEPA, 2000; Tardy et al., 2003; Wright et al., 2002, 2003, 2004). It is particularly suited to the stabilization of Pb due to the highly insoluble nature of the pyromorphite phase formed by the reaction of Pb with phosphate ions in solution (USEPA, 2000; Tardy et al., 2003; Wright et al., 2004). The solubilities of a wide range of other metals are also reduced upon



formation of phosphate compounds. Reactions occur in the aqueous phase and result in the precipitation of the relatively insoluble metal phosphate products.

The post MCD™ metal stabilization makes use of PIMS through the addition of Apatite II™, a phosphate product derived from fish bones. Stabilization of metals in contaminated soils is achieved by the addition of Apatite II™ at 1% to 5% (by wt), along with a sufficient quantity of water. Intimate mixing of contaminated soil, Apatite II™ and water is easily achieved through a pug mill or similar mixing device located after the MCD™ reactor. TCLP concentrations for the soil should be reduced to well below the target SAC of 5 mg/l for Pb. The stabilization of other metal contaminants to below TCLP SAC should also occur. The use of the STLC test in California for the leaching of metals may make other stabilizing agents such as lime/cement more affective in this application.



#### 4.0. Characteristics of Contaminated Soil in Stockpiles 5, 6 and 7

The soil in PCB Hotspot Stockpiles 5, 6 and 7 is a mix of sand, sandy loam, silt and clay excavated from the PCB Hotspot area of HPS. Each stockpile contains approximately 3,000 ton of contaminated soil. The maximum PCB (exclusively Arochlor 1260) concentration in these stockpiles is 170,000 µg/kg. Stockpiles are also contaminated with heavy metals (mainly Pb and Cu) and petroleum hydrocarbons (diesel and motor oil), along with a many other minor contaminants.

A list of the concentration of contaminants detected in the three baseline stockpile soil samples collected for this trial is provided below. The soil samples used in the TS were taken from these stockpiles by the Navy. Soil samples 01 through 03 were taken from stockpile 5, 04 through 06 from stockpile 6, and 07 through 09 from stockpile 7. Soil samples are stated by the Navy to be representative of the range of PCB and metal contamination levels and soil types present in PCB Hotspot Stockpiles 5, 6 and 7.

**Table 1. List of Contaminants for PCB Hot Spot – Soil Stockpiles 5, 6 and 7.**

Contaminant	Maximum Concentration (mg/kg)		
	Stockpile 5	Stockpile 6	Stockpile 7
PCBs	78	170	51
4,4'-DDT	1.0	2.1	-
TPH-d	1,300	3,800	1,000
TPH-mo	2,100	5,000	1,800
Antimony	15	21	46
Barium	110	180	130
Chromium	220	170	270
Copper	2,800	1,900	2,200
Lead	1,500	2,100	870
Nickel	160	140	140
Zinc	1,300	1,300	1,400



5.0 Treatability Study Operations

5.1. Stage 1 – MechanoChemical Destruction of PCBs

Stage 1 of the TS evaluated the effectiveness of the MCD™ technology in remediating PCB contaminated soil to <1,000 µg/kg. The main operations of the TS are shown schematically here with further detail below.

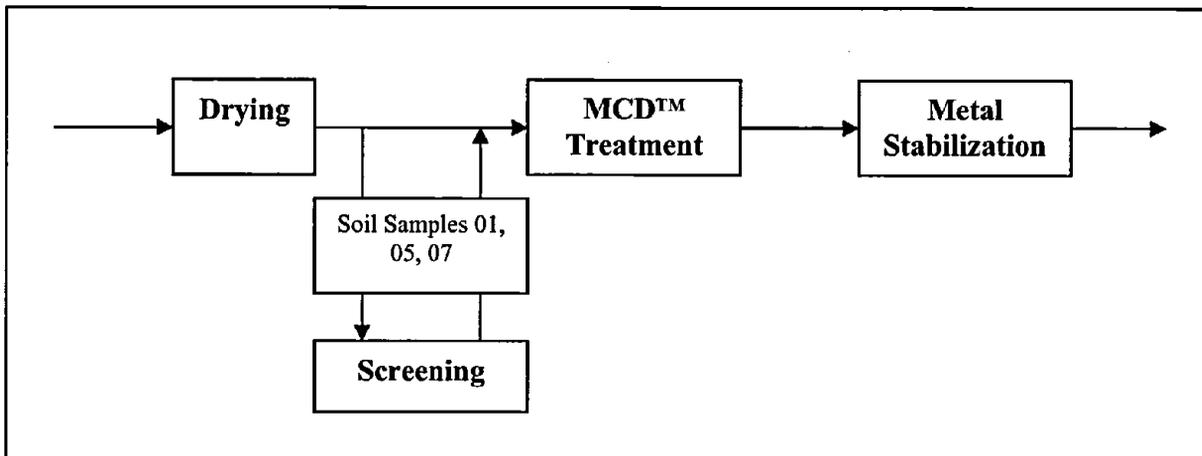


Figure 1. Treatment Sequence Schematic.

5.1.1. Stage 1, Phase 1 – Soil Drying

The objective of the soil drying phase was to minimize the moisture content of the soil samples prior to MCD™ treatment. The mean moisture content in the 9 soil samples as received was 12.7%. The moisture content in each soil sample prior to drying is shown in the table below.

Table 2. Moisture content of as received soil samples.

	Sample 01	Sample 02	Sample 03	Sample 04	Sample 05	Sample 06	Sample 07	Sample 08	Sample 09
Moisture	9%	23%	28%	10%	8%	8%	8%	12%	8%

The negative influence of moisture on grinding efficiency in dry grinding operations is well established (Perry & Green, 1984). Grinding efficiency has a direct influence on the generation of active surface species (Si and Si-O) and hence on the rate of MC destruction reactions. A small thermostatically controlled incubator was used to dry Soil Samples 01 through 09 to <2% moisture content. The incubator was controlled to a maximum temperature of 55°C to ensure



effective drying of the soil while minimizing the volatilization of PCB contaminants. Drying was conducted within an exclusion zone in Building 414 at HPS.

Following drying, one soil sample from each PCB Hotspot Stockpile was selected for screening. The selected soil samples, 01, 05 and 07, were hand screened to generate <5 mm and >5 mm particle size fractions. The exercise was to determine the level of contamination reduction on the >5 mm fraction. The >5 mm fraction was reconstituted with the <5 mm fraction prior to MCD™ Treatment. The >5 mm fraction contained on average 8% (by wt) of the total dry weight of the samples screened.

A sample of each dried soil sample was taken to confirm that PCB losses in the drying process were insignificant and to give baseline results for calculation of the destruction efficiency achieved in the MCD™ reactor.

In summary, the operational steps for soil drying were as follows:

1. All soil samples (01 through 09) were individually dried in the incubator at 55°C for a total of 24 to 27 hours.
2. Selected dried soil samples (01, 05 and 07) were screened to separate off the particle size fraction greater than 5 mm for PCB and metal analysis. Soil samples were re-constituted prior to MCD™ treatment.
3. All dried soil samples were sampled for chemical analysis to give an untreated PCB concentration prior to MCD™ treatment

### ***5.1.2. Stage 1, Phase 2 – MCD™ Treatment***

The objective of the MCD™ treatment phase was to mechanochemically destroy the PCB contaminants in the soil to <1,000 µg/kg.

Dried soil samples were processed individually in the pilot Series III MCD™ reactor in order of increasing PCB concentration (according to baseline concentrations as shown in Table 1, Section 2.4). Soil samples were mixed with selected proprietary reagents (1% by wt) and quartz sand (5% by wt). A further 5% (by wt) of quartz sand (10% total) was added to Soil Sample 06 which had the highest PCB concentration. Each soil sample received a total of 45 minutes MC treatment in the MCD™ reactor. Samples for chemical analysis were collected at 15, 30 and 45 minutes. Following the extraction of each 45 minute sample, the MCD™ reactor continued to operate until



all the soil had discharged from the reactor. Once material flow ceased, an additional run period was continued until no evidence of the previous sample could be observed.

In summary, the operational steps are as follows:

1. Each dried soil sample was weighed and 1% (by wt) premixed proprietary reagents and 5% (by wt) quartz sand were mixed in. Soil Sample 06 had a further addition of 5% (by wt) quartz sand prior to MCD™ treatment.
2. The prepared soil/reagent mix was then treated in the MCD™ reactor for a total of 45 minutes with samples for chemical analysis collected after 15, 30 and 45 minutes.
3. The MCD™ reactor continued to operate after full discharge of MCD™ treated soil in preparation for the following soil sample.

## 5.2. Stage 2 – Stabilization of Metals

The aim of the metals stabilization stage was to reduce the TCLP concentration of Pb to <5 mg/l. Apatite II™ was used to facilitate phosphate induced stabilization of metals.

Following MCD™ treatment, 5% (by wt) Apatite II™ was added to each soil sample along with sufficient water to facilitate stabilization reactions. Each soil sample was rotated in a mixer bowl for 15 minutes to ensure intimate contact between the Apatite II™ and the metal contaminants and to allow stabilization reactions to occur. The stabilization step yielded a dust free reconstituted product similar in appearance to the original soil samples.

In summary, the operational steps were as follows:

1. Soil Samples 01, 05, 06, 07 and 08 were selected for metals sampling and analysis (one or two samples from each stockpile). After 15 minutes of MCD™ treatment for these soils, samples were collected for metals analysis.
2. MCD™ treated soil samples were weighed and 5% (by wt) Apatite II™ was added.
3. The soil/Apatite was rotated in the sealed mixer bowl for 2 minutes to disperse the Apatite through the soil prior to addition of water.
4. Water was added to the soil/apatite and the mixing bowl rotated for 15 minutes to facilitate stabilization of metals and to restore the soil to pre-drying moisture content (~10%) and appearance.



5. At the conclusion of each stabilization trial the mixer was emptied and cleaned in preparation for the following trial.

### 5.3. *Soil Sampling*

Soil samples were collected during the TS as follows.

1. Baseline samples from PCB Hotspot Stockpiles 5, 6 and 7 and from TS Soil Samples 01 through 09 were collected and analyzed prior to the TS. Samples were analyzed for TPHs (EPA Method 8015B), VOCs (EPA Method 8260B), SVOCs (EPA Method 8270C), OCPs (EPA Method 8081A), PCBs (EPA Method 8082) and total, TCLP and STLC metals (EPA Methods 1311, CAL-WET & 6010B).
2. Dried soil samples were taken after drying of each TS Soil Sample. Coarse fraction (>5 mm) dried soil samples were collected for TS Soil Samples 01, 05 and 07 following screening. All samples were analyzed for PCBs (EPA Method 8082) with samples 01, 05, 06, 07 and 08 also analyzed for OCPs (EPA Method 8081A). Dried soil samples 02, 05, 06 and 07 were analyzed for total organic carbon (TOC) (USEPA Lloyd Kahn Method). Dried soil samples 02, 04, 05 and 06 were analyzed for soluble chloride (EPA Method 300.0).
3. MCD™ treated samples were taken after 15, 30 and 45 minutes of MCD™ treatment for each TS Soil Sample. All samples were analyzed for PCBs (EPA Method 8082). 15 minute MCD™ treated samples for Soil Samples 01, 05, 06, 07 and 08 were analyzed for OCPs (EPA Method 8081A) and total, TCLP and STLC metals (EPA Methods 1311, CAL-WET & 6010B). 15 minute MCD™ treated samples 02, 05, 06 and 07, and 45 minute MCD™ treated samples 05 and 07 were analyzed for TOC (USEPA Lloyd Kahn Method). 15, 30 and 45 minute MCD™ treated samples 02 and 06, 15 and 45 minute MCD™ treated sample 05, and 45 minute MCD™ treated sample 07 were analyzed for soluble chloride (EPA Method 300.0).
4. Metal Stabilized samples were taken after metal stabilization treatment for TS Soil Samples 01, 05, 07 and 08. Samples were analyzed for TCLP and STLC metals (EPA Methods 1311, CAL-WET & 6010B). Total metals analysis was not performed on these samples.



#### 5.4. *Waste Management*

All treated soil, disposable items, and PPE (excluding laboratory samples) were sealed in containers and/or disposable bags and subsequently collected from Building 414 for appropriate disposal by the Navy.

#### 5.5. *Project Time Line*

The TS was completed according to the time line in the table below. Only one minor delay occurred in the TS during MCD™ treatment of the first soil sample (Soil Sample 03) when the MCD™ reactor was found to be operating outside the operational criteria with respect to reactor RPM and mechanical energy intensity. Hence the 15 minute sample (MCD03-15) was treated under these abnormal operational conditions. Further operation was postponed while appropriate mechanical adjustments were made to the engineering parameters of the MCD™ reactor to bring it back within the operating specifications, determined previously through the R&D program. The increase in MCD™ reactor RPM between 15<sup>th</sup> and 16<sup>th</sup> May was approximately 10%. A further 10% increase reactor RPM was achieved between 16<sup>th</sup> and 17<sup>th</sup> May.



**Table 3. MCD™ Treatability Study timeline.**

Date	Stage, Phase	Description of Work
2 <sup>nd</sup> – 12 <sup>th</sup> May	Set up Stage 1, Phase 1	Setting up health and safety requirements and drying of soil samples.
13 <sup>th</sup> May	Stage 1, Phase 1	Screening of Soil Samples 01, 05 and 07.
15 <sup>th</sup> May	Set up	Deployment of MCD™ reactor and trial equipment on site at Building 414 and establishment of the MCD™ Trial Exclusion Zone, as defined in the Program Health & Safety Plan (PHSP).
15 <sup>th</sup> May	Stage 1, Phase 2	MCD™ treatment of Soil Sample 03 begins. MCD™ reactor operating outside design parameters. Trial postponed for mechanical adjustments to bring MCD™ reactor within operating within design specifications.
16 <sup>th</sup> May	Stage 1, Phase 2	MCD™ treatment of Soil Samples 03, 09, 08 and 07 completed.
17 <sup>th</sup> May	Stage 1, Phase 2	MCD™ treatment of Soil Samples 01, 05, 04, 02 and 06 completed.
18 <sup>th</sup> May	Stage 2	Metal stabilization of Soil Samples 01, 05, 06, 07 and 08.
19 <sup>th</sup>	Pack up	Pack up and store MCD™ reactor and trial equipment.
19 <sup>th</sup> May – 2 <sup>nd</sup> June	Analysis	Analysis of samples at Curtis & Tompkins Ltd.
25 <sup>th</sup> May – 25 <sup>th</sup> June	Reporting	Preparation of final trial report.



### 6.0 Treatability Study Results

The TS was divided into two parts, MCD™ treatment of PCBs, and phosphate induced stabilization of metals. In summary, the MCD™ treatment was a success with residual PCB concentration <1,000 µg/kg in all treated samples. MCD™ treatment also resulted in acceptable TCLP Pb concentrations, <5 mg/l in all treated samples. This made the phosphate stabilization step largely redundant. The detailed results are presented below. A full set of analytical results from Curtis & Tompkins Ltd., including gas chromatograms for untreated and MCD™ treated samples, are available electronically on request.

#### 6.1 Pre-Treatment Drying and Screening Results

The influence of the drying and screening pre-treatment steps are illustrated in the figure below. The PCB concentration in dried samples is generally similar to baseline concentrations, with the exception of samples 03 and 06. Sample 03 is a clay sample which had a low baseline PCB concentration of 10,000 µg/kg. Drying may help to improve the extraction efficiency by breaking up the clay. Sample 06 has the highest baseline PCB concentration and the lower result for the dried sample may be more representative due to homogenization during the drying stage.

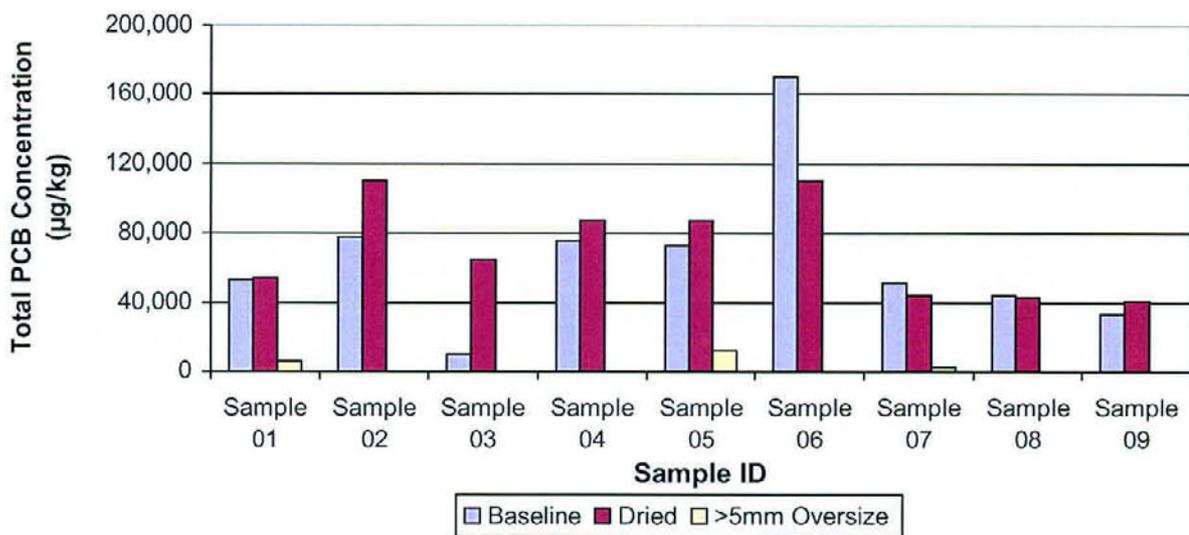


Figure 2. Influence of Pre-Treatment on PCB Concentration.

## 6.2. MCD™ Treatment Results

### 6.2.1. PCBs

The results for each individual Soil Sample are shown in the figure below. Extending the MC treatment beyond 15 minutes does not appear to reduce PCB concentrations significantly. Several samples have PCB concentrations below the detection limit of 15 µg/kg.

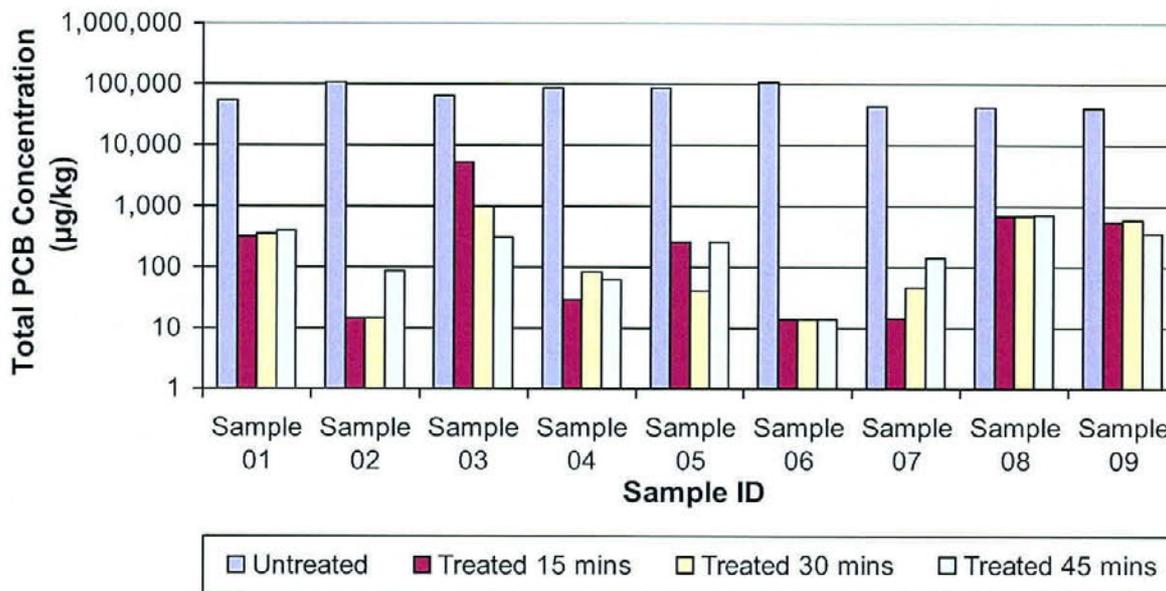
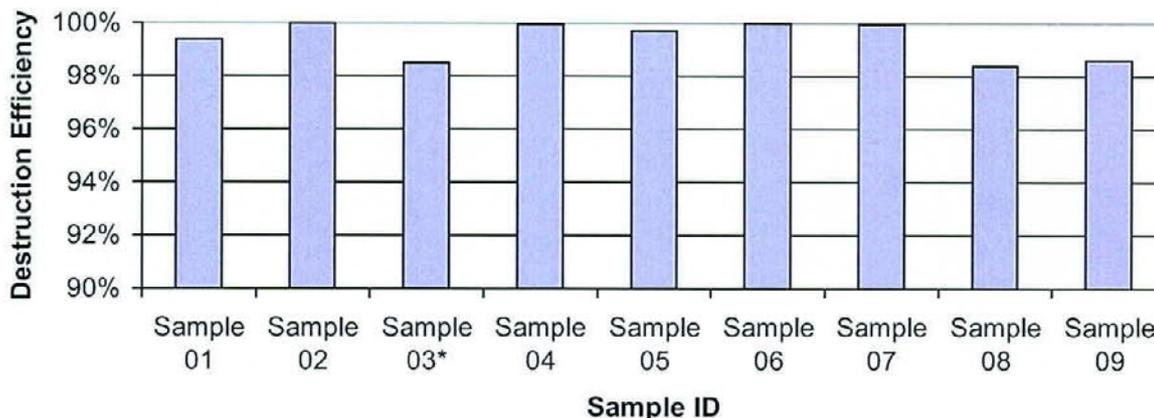


Figure 3. MCD™ treatment of PCB contaminated soil samples.

Destruction efficiency after 15 minutes of MCD™ treatment is >98.4% for all Soil Samples as shown below. Several samples have DE approaching 100%.

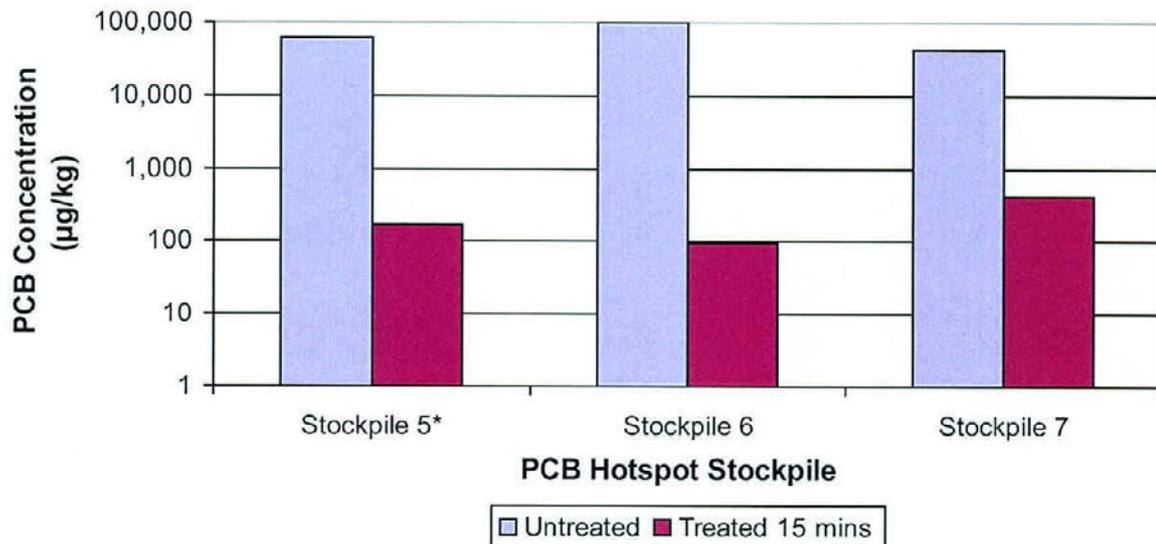


\* 30 minute sample used to calculate DE as MCD™ reactor operation outside design parameters for 15 minute sample

Figure 4. Destruction efficiency achieved after 15 minutes of MCD™ treatment.



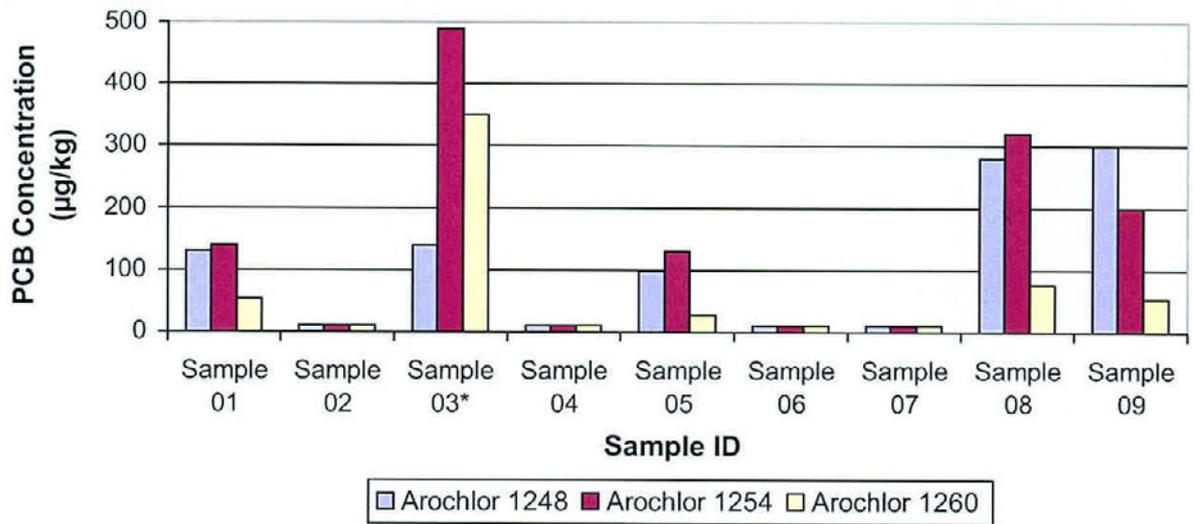
The results for each soil sample can be combined to give mean untreated and MCD™ treated results for the individual PCB Hotspot Stockpiles 5, 6 and 7. Soil samples 01 – 03, 04 – 06 and 07 – 09 correspond to Stockpiles 5, 6 and 7 respectively with the 15 minute results used.



\* Sample 03 omitted from calculation as MCD™ reactor operation out of specification

**Figure 5. Mean untreated and treat PCB concentrations in each stockpile.**

The relative concentrations of the three different Arochlors detected in the treated samples are shown below. Similar distributions were seen for 30 and 45 minute samples. In Samples 01, 05, 08 and 09 with the MCD™ reactor under normal operating conditions, the concentration of Arochlors 1248 and 1254 were significantly higher than that of Arochlor 1260. Arochlor 1248 and 1254 in the untreated samples were less than the detection limit (<960 to <2,500 µg/kg). Hence it is unknown how much, if any, Arochlor 1248 and 1254 was present in untreated samples, except that concentrations are below the detection limits mentioned above.



\* 30 minute result used

Figure 6. Arochlor concentrations after 15 minutes of MCD™ treatment.



### 6.2.2. OCPs

The OCP results for individual samples are shown in the figure below. DDT was detected in all untreated samples and dieldrin was only detected in three of the five untreated samples. DDT concentration was reduced to below the detection limit in all MCD™ treated samples (<17 µg/kg). Dieldrin was also reduced to below the detection limit in the three samples in which it was initially detected.

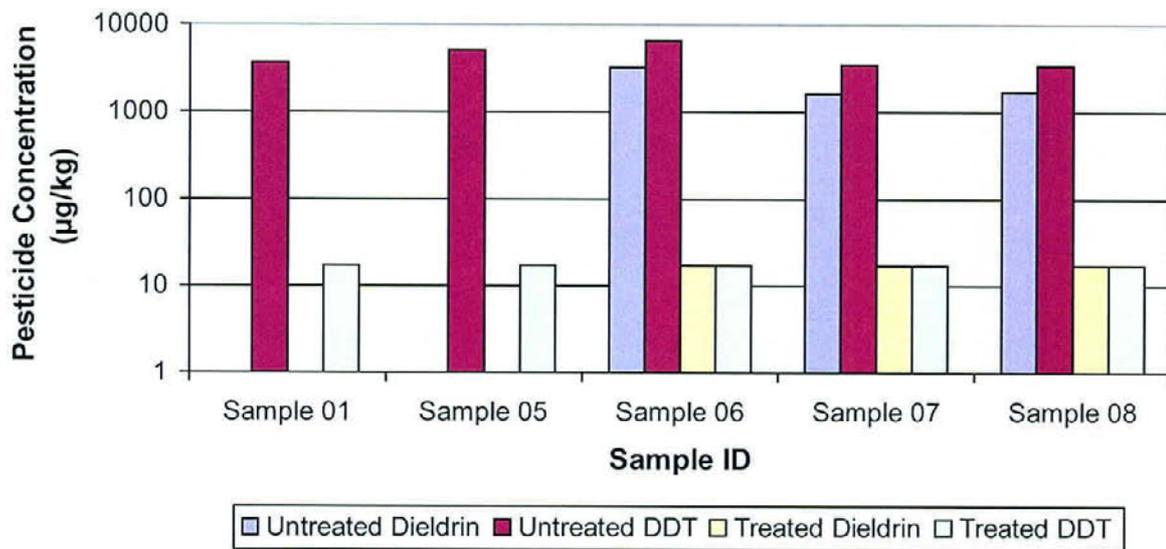
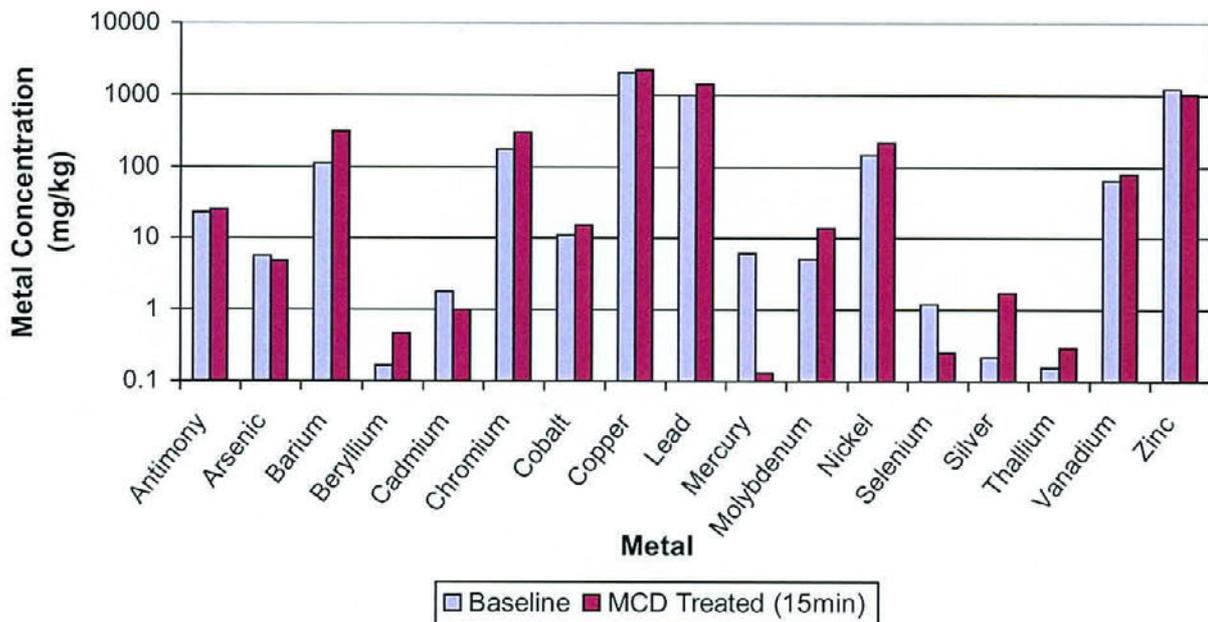


Figure 7. MCD™ treatment of pesticides PCB contaminated soil samples.

### 6.3. Metal Stabilization Results

The metal contamination in the TS samples is secondary to the PCB contamination, and metal stabilization is generally regarded as a well established remediation technology. Hence, for simplicity and brevity the individual metal results for the soil samples analyzed for metals (samples 01, 05, 06, 07 and 08) are combined and shown as the mean concentration. The total metal concentrations in baseline and MCD™ treated (15 minutes) soil samples are shown below.



**Figure 8. Metal contamination pre and post MCD™ treatment**

The TCLP metal results for baseline, MCD™ treated and stabilized samples are shown below. The means for baseline results are calculated from Stockpile 5 and 6 sample results (6 samples from each stockpile) supplied by the Navy. The means for the MCD™ treated and stabilized samples are calculated from the 5 soil samples analyzed (Soil Samples 01, 05, 06, 07 and 08). The TCLP concentrations of arsenic, beryllium, cadmium, chromium, mercury, molybdenum, selenium, silver, thallium and vanadium are generally below the detection limits for these compounds (<0.002 mg/l for mercury, <0.02 mg/l for beryllium, 0.1 mg/l for vanadium, <0.05 mg/l for others) and hence they are not shown in the figure below.

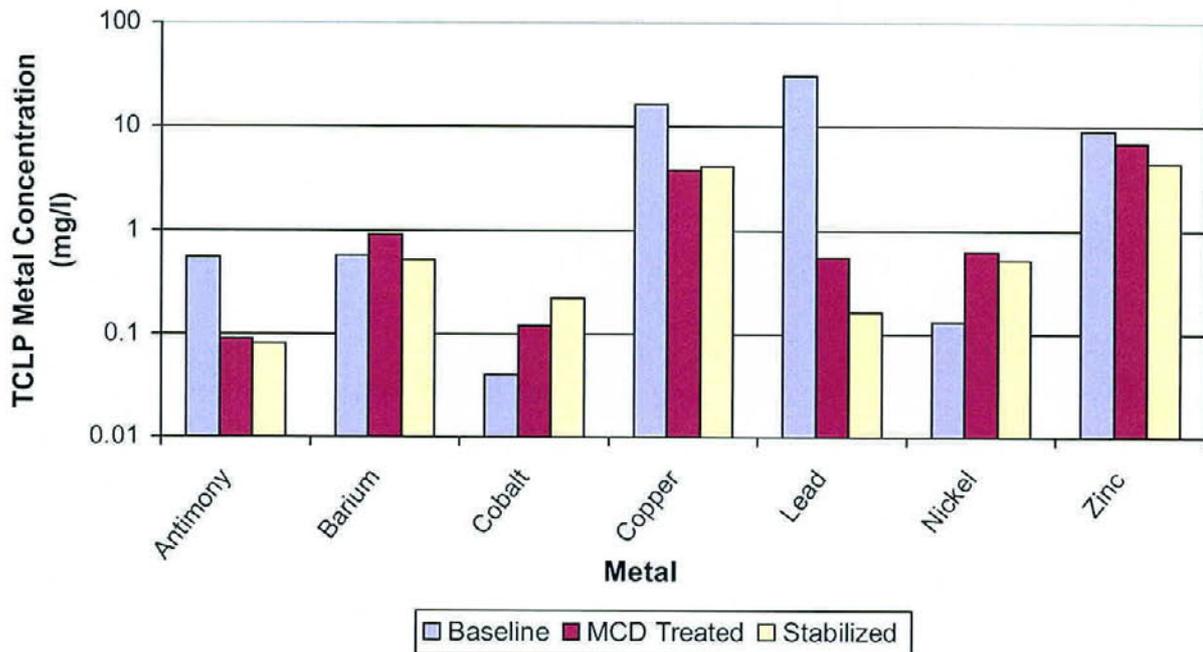


Figure 9. TCLP analysis results for baseline, MCD™ treated and stabilized samples.

The STLC metal results for baseline, MCD™ treated and stabilized samples are shown below. The means for baseline results are calculated from Stockpile 5 and 6 sample results (6 samples from each stockpile) supplied by the Navy. The means for the MCD™ treated and stabilized samples are calculated from the 5 soil samples analyzed (Soil Samples 01, 05, 06, 07 and 08). The STLC concentrations of arsenic, beryllium, cadmium, mercury, molybdenum, selenium, silver and thallium are generally below the detection limits for these compounds (<0.002 mg/l for mercury, <0.1 mg/l for beryllium, <0.25 mg/l for others) and hence they are not shown in the figure below.

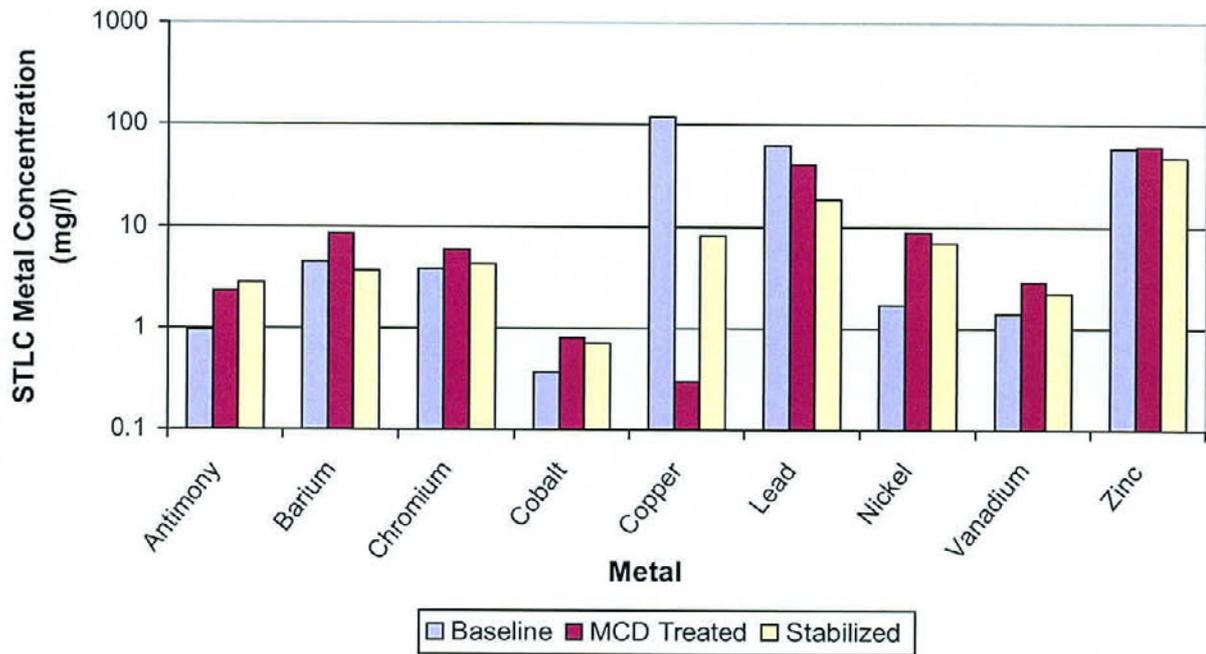


Figure 10. STLC analysis results pre and post stabilization.

#### 6.4. Inorganic Chloride and Total Organic Carbon

The TOC results show a significant reduction in TOC on MC treatment with only 28% to 62% remaining after 15 minutes. The TOC continues to reduce on further MCD™ treatment but at a slower rate.

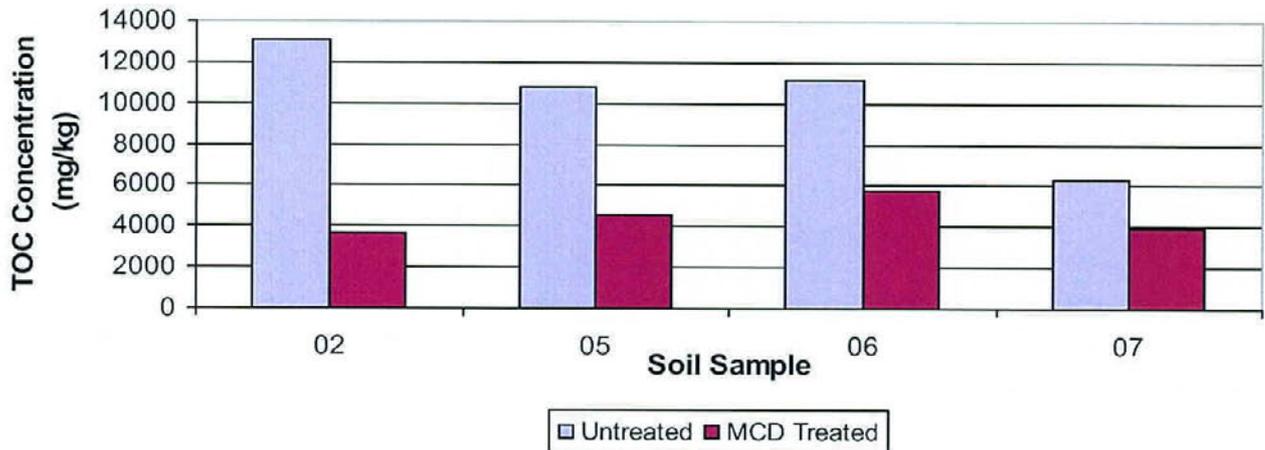


Figure 11. TOC concentration before and after MCD™ treatment (for 15 minutes).

The amount of soluble inorganic chloride in samples also reduces during MCD™ treatment as shown in the figure below. Soil samples 04 and 05 only had a single MCD™ treated sample analyzed (15 mins for 04 and 45 mins for 05) in addition to the untreated sample. Hence the absence of data for the other MCD™ treatment times is for this reason.

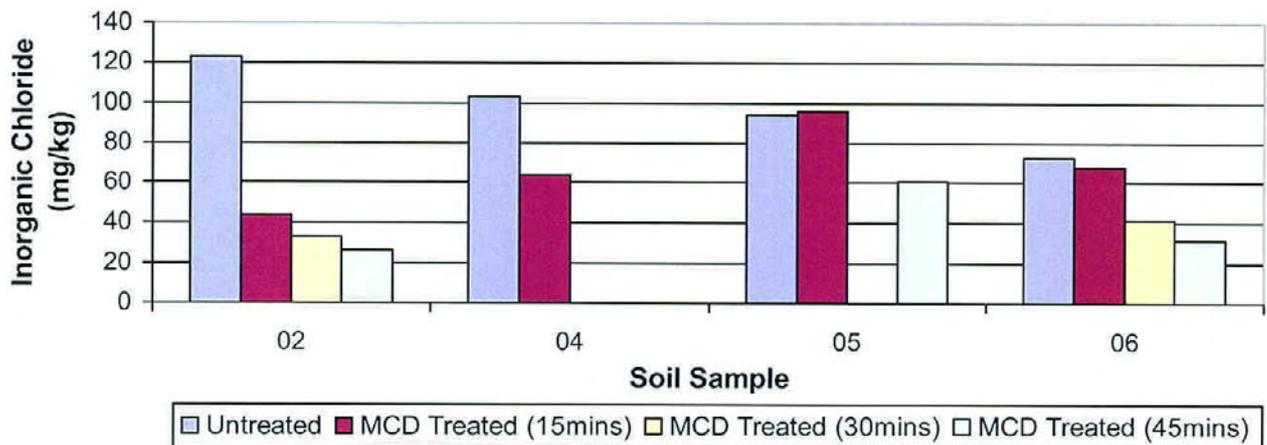


Figure 12. Inorganic chloride concentration before and after MCD™ treatment.



## 7.0 Discussion of Treatability Study Results

The TS was conducted during May 2006 by Shaw and EDL using the pilot Series III MCD™ reactor and associated trial equipment. Nine 25kg soil samples taken from HPS PCB Hotspot Stockpiles 5, 6 and 7 were treated in a two stage process involving MCD™ treatment of PCBs and phosphate stabilization of heavy metals. Sample sets taken include Baseline (supplied by the Navy), Dried, MCD™ Treated and Apatite II™ stabilized. Samples were analyzed for PCBs, OCPs, and metals (total, TCLP, STLC) to provide information on the change in contaminant concentration. The results of the analyses are summarized in Section 6.0. The full analytical results are included in Appendix A and original analytical laboratory reports from Curtis & Tompkins Ltd. are available in electronic form on request from Shaw/EDL. The following sections provide a discussion of the results of the TS. Conclusions and recommendations based on these results are included in Section 8.0.

### 7.1. *Stage 1, Phase 1 – Pretreatment Drying and Screening*

Stage 1, Phase 1 of the TS was conducted from 2 – 12 May, 2006 using the nine 25kg soil samples taken from HPS PCB Hotspot Stockpiles 5, 6 and 7 supplied by the Navy. The average moisture content of soil samples as received was 12.7%. The drying procedure reduced the moisture content to <2% to enable efficient MCD™ treatment of the soil samples. The drying was performed in an incubator with the temperature controlled to a maximum of 55°C to minimize the volatilization of PCBs. Each soil sample required 24 – 27 hours in the incubator to reduce the moisture content to below the target.

Screening of selected dried soil samples (samples 01, 05 and 07) was performed to determine the location of the contaminants with respect to soil particle size. Contamination is usually concentrated in the fine fraction of soil particles and hence it may be possible to reduce the mass of contaminated soil requiring remediation by screening off the larger particle sizes. This is a key part of the remediation strategy employed by EDL at the Mapua site, where the volume of soil requiring treatment in the MCD™ plant is reduced by 10% – 15% by screening off the >5mm fraction. This is possible with the contamination level in the resulting the >5 mm fraction being typically an order of magnitude below the SAC of 200 mg/kg DDT for onsite burial below 3ft.

Although a reduction in PCB concentration was achieved in the three coarse fractions (>5 mm) analyzed, the residual PCB concentration was still above the target SAC for the TS of



1,000 µg/kg. The PCB concentration in the screened >5 mm coarse fraction for Soil Samples 01, 05 and 07 was between 6% and 14% of the PCB concentration in the unscreened dried soil with a mean across the three samples of 6,930 µg/kg. The coarse fraction (>5 mm) represents approximately 8% of the total mass in the PCB Hotspot samples screened.

The PCB concentration in the dried soil samples was similar to that measured in the baseline samples with the exception of Samples 03 and 06. Sample 03 had the lowest baseline PCB concentration (10,000 µg/kg) while Sample 06 had the highest (170,000 µg/kg). Hence these extreme baseline PCB concentrations may not be representative of the mean concentration in the soil samples.

## ***7.2. Stage 1, Phase 2 – MCD™ Treatment***

### ***7.2.1. PCBs Overall***

The MCD™ treatment of HPS PCB Hotspot soil samples in the pilot Series III MCD™ reactor was successful. The aim SAC of <1,000 µg/kg PCBs was achieved in all soil samples when the MCD™ reactor was operating within specification<sup>2</sup>. Destruction efficiencies >98.4% were achieved for all samples. In several cases destruction efficiency >99.95% was achieved within 15 minutes (Soil Samples 02, 04, 06, 07).

MCD™ treatment beyond the initial 15 minutes does not appear to give significant benefit based on the TS results, with several 30 and 45 minute samples giving higher PCB concentrations. This is in contrast to extensive laboratory research which has indicated that MC destruction of organic contaminants follows pseudo-first order reaction kinetics (EDL, unpublished research). This being the case, with ~99% destruction after 15 minutes, the amount of PCB destroyed in subsequent 15 minute intervals will be in the parts per billion range. Sampling at more frequent intervals when destruction is less advanced should give better data for determining reaction kinetics.

### ***7.2.2. OCPs***

Five soil samples were analyzed for OCPs before and after MCD™ treatment. The indiscriminate nature of the MCD™ process with respect to destruction of organic contaminants is illustrated here with DDT destroyed to below detection limits (<17 µg/kg) in all MCD™ treated samples.



Dieldrin, detected in three of the five untreated soil samples was also destroyed to below the detection limit (<17 µg/kg). DE was >99.5% for DDT and >98.9% for dieldrin (in soils initially containing dieldrin). These DE results are restricted by the detection limit of the analysis and in reality will be higher.

### **7.2.3. Final Products**

Based on the results of previous research by EDL and other independent parties (EDL, unpublished research; Hall et al., 1996; Zhang et al., 2001, 2002; Ikoma et al., 2001; Tanaka et al., 2003a, 2003b, 2004; Heineke, 1984; Field et al., 1997; Kaupp et al., 2002, 2003, 2005), organic compounds, including PCBs, are transformed into a high molecular weight amorphous carbon product and inorganic chloride during MC treatment. The reduction in TOC in samples on MC treatment during the TS suggests that the amorphous carbon product then goes on to form CO<sub>2</sub> and carbonates, and maybe other carbon products not detectable by TOC. The formation of CO<sub>2</sub>, carbonates, carbides and other carbon containing compounds during MC treatment is well established (EDL, unpublished research; Heineke, 1984; Kalinkin et al., 2004; Lin & Nativ, 1979; Tkacova, 1989; Gaffet et al., 1999; Gilman, 1996). The inorganic chloride already in the soil and released from the PCBs is bound to the mineral compounds in the soil matrix and is not extractable as soluble chloride. The chloride issue is discussed further in section 7.2.5 below.

### **7.2.4. Intermediate Breakdown Products**

Analysis of untreated samples gives Arochlor 1248 and 1254 concentrations below detection limits of between 960 and 2500 µg/kg. These high detection limits are due to the mg/kg concentration of Arochlor 1260 in the untreated samples. In treated samples, after >99% destruction of Arochlor 1260, much lower detection limits apply and Arochlors 1248 and 1254 are detected at µg/kg level. With these analyses it is impossible to know whether the absolute concentrations of Arochlors 1248/1254 increase, decrease or stay the same between untreated and MCD™ treated samples. What is obvious is the vastly increased ratio of Arochlors 1248/1254 to Arochlor 1260 in MCD™ treated samples compared to untreated samples. This could occur in two ways. Either, Arochlors 1248/1254 were present in untreated samples and were not, or only very slowly destroyed during MC treatment. Or, Arochlors 1248/1254 were formed as breakdown products through dechlorination of Arochlor 1260 during MC treatment.

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<sup>2</sup> MCD reactor was operating out of design specification with respect to MCD reactor rpm and mechanical energy



Based on EDL research the first possibility is extremely unlikely as organic compounds with the same carbon skeleton have similar ionization energies and free radical stability. This is confirmed by the comparative MC destruction rates of DDT and DDD, of PCP and HCB, and of various PAHs (EDL, unpublished research). Hence the MC destruction rate of Arochlors 1248, 1254 and 1260 should be similar. Dechlorination is one of several MC reaction mechanisms as confirmed during MC treatment of a range of organochlorines (DDT, DDD, HCB, PCP) (EDL, unpublished research). The presence of the lesser chlorinated PCBs in some MCD™ treated samples is therefore consistent with previous research and an indication that MC reactions have occurred. These lesser chlorinated PCB breakdown products are also susceptible to MC destruction based on the research cited in section 3. Arochlor 1248/1254 PCBs are therefore only intermediate products where MC destruction is allowed to proceed to completion as in several samples where Arochlors 1248/1254/1260 are not detected. In the samples where they are detected the MC reactions have not proceeded to completion.

EDL research has shown the following with respect to intermediate breakdown products (EDL, unpublished research). Overall, few intermediates are detected during mechanochemical treatment of organic compounds. Destruction directly to the final high molecular weight amorphous carbon product dominates. Primary intermediate forming reactions are dechlorination, scission of aliphatic C-C bonds and opening of aromatic rings. The maximum yield of closely related intermediates (i.e. direct dechlorination through loss of 1 chlorine) formed during MCD™ treatment is typically <1% of original compound. Intermediates requiring more than one reaction step (i.e. loss of 2 chlorines) reach maximum concentrations <0.1% of original compound. All intermediates are destroyed as MCD™ treatment progresses, but may be present at detectable levels until almost all the original starting compound is destroyed. Greatest yield of intermediates generally occurs when destruction of starting compound is ~80%. With >99% destruction achieved in most of the MCD™ treated samples, concentration of intermediates will be much less than the maximum. The lack of dechlorination products in MCD™ treated Samples 02, 06 merely reflects the degree of PCB destruction achieved in the samples (>99.97%). Hence reduction in PCB concentration (i.e. mechanochemical destruction to high molecular weight amorphous carbon and inorganic chloride) without the observance of many intermediates is consistent with all EDL research to date.

intensity for the initial 15 minutes while processing Soil Sample 03. Hence the 15 minute result for Soil Sample 03 is not representative of design operating specifications.



### 7.2.5. Chloride Balance

The low starting PCB concentrations (<100 mg/kg), the binding of chloride in the inorganic soil matrix (silicates...) and the variable ambient inorganic chloride concentration in the soil samples makes a meaningful chloride balance difficult to achieve. Arochlor 1260 PCBs contain 60% chloride (by wt) and hence if all the chloride was released as inorganic chloride the concentration would increase by <60 mg/kg. This is generally less than the existing chloride concentration in the untreated soil samples which ranged from 59 to 123 mg/kg. The main difficulty however arises from the binding of the chloride and the inability of the soluble chloride analysis to account for this.

The chloride concentration in the untreated samples is greater than in the treated samples and chloride concentration decreased with increasing treatment time. This decrease in chloride ion concentration with treatment time is consistent with other results obtained by EDL. MC treatment of naphthalene and sodium chloride in quartz sand showed a gradual reduction in inorganic chloride concentration as MC treatment time increased (>70% reduction at the conclusion of milling). XPS analysis did not detect any C-Cl bonds, hence the chloride is progressively incorporated into the amorphous silicate formed during MC treatment of quartz. A similar result was obtained during MC treatment of charcoal and sodium chloride in quartz sand (EDL, unpublished research). Theoretically the chloride yield from PCB destruction should have increased the chloride concentrations for the samples analyzed by 54% to 90%. But the binding of the chloride ions observed makes this soluble chloride analysis inappropriate in this application. Hence these results cannot confirm that release of inorganic chloride occurred during MCD™ treatment of the PCBs. An alternative analytical technique capable of detecting all forms of chloride is necessary for conclusive evidence of inorganic chloride production from PCBs during MCD™ treatment.

### 7.2.6. Quartz Sand

Analysis of baseline and dried samples for soil sample 06 gave PCB concentrations of 170,000 µg/kg and 110,000 µg/kg respectively. These high concentrations led to the addition of a further 5% (by wt) quartz sand, on top of the usual 1% reagents and 5% quartz sand addition. PCB concentrations were below detection limits (<9.6 µg/kg) for all treated samples giving a DE of 99.99%. This is the highest DE achieved in the TS and better than for the other two soil samples taken from Stockpile 6 (DE 99.70% to 99.98% across treated samples). While not altogether conclusive, it does fit with EDL research indicating the benefit of higher quartz content



and with the accepted MC destruction mechanism being primarily Si<sup>•</sup> and Si-O<sup>•</sup> radicals (Kaupp et al., 2002, 2003).

#### **7.2.7. Reactor RPM**

The order in which samples were treated is also illuminating given the fact that the operation of the pilot MCD™ reactor was adjusted as the TS progressed. This fine tuning led to an increase in MCD™ reactor RPM of approximately 10% each day. With MCD™ reactions dependent on the input mechanical energy intensity (reactor RPM), the rate and extent of reaction increase with reactor RPM. This is generally what occurs with a trend toward lower residual PCB concentration as the TS progressed. MCD™ treatment order, based on increasing baseline PCB concentration was: Day 1 – Sample 03; Day 2 – Samples 03 cont', 09, 08, 07; Day 3 – Samples 01, 05, 04, 02, 06.

Soil sample 03 was the first soil sample treated in the MCD™ reactor in the TS. The MCD™ reactor was operating outside its design specification with respect to reactor RPM and mechanical energy intensity prior to the 15 minute sample (MCD03-15) being taken. This resulted in the postponement of MCD™ treatment of Soil Sample 03 while the mechanical set up of the MCD™ reactor was adjusted. When the remaining samples were taken the MCD™ reactor was operating within the design specifications (400 – 600 rpm). The 30 minute result (MCD03-30) is below the 1,000 µg/kg target but higher than all other MCD™ treated results due to the ongoing effect of the MCD™ reactor operating out of specification. This high MCD03-15 result illustrates the importance of MCD™ reactor speed which has a significant influence on the mechanical energy intensity and destruction performance (EDL, unpublished research). This relationship has been mathematically modeled (see section 7.4 below) and is precisely why EDL designed and built the high energy Series III MCD™ reactor used in the TS.

#### **7.2.8. Volatilization**

PCBs are semi-volatile compounds which volatilize very slowly under ambient conditions. Volatility (vapor pressure) increases with temperature up to the boiling point, which for Arochlor 1260 PCBs is between 350°C and 420°C. The operating temperature of the MCD™ reactor is well below the boiling point range but is also higher than ambient due to the dissipation of mechanical energy as heat. Hence volatilization of PCBs will occur in the MCD™ reactor.

The important issue however is not whether volatilization occurs, but whether volatilized PCBs are released from the MCD™ reactor prior to MC destruction. Extensive research by EDL and other independent parties in totally closed laboratory systems indicates that MC destruction of



organics does occur. In these experiments there is no opportunity for release of volatilized compounds and a variety of analytical techniques have been employed to confirm the presence of amorphous carbon and inorganic chloride final products (Field et al., 1997; Kaupp et al., 2002; Tanaka et al., 2003; EDL, unpublished research). Analysis of headspace samples during EDL research into MC destruction of DDT reveals only small amounts of DDT (and metabolites) in the gas phase at intermediate stages of MC treatment and no DDT (or metabolites) in the gas phase at the conclusion of MC treatment (residual DDT concentration in solid <0.1% of original), despite the elevated temperature of the system (~100°C).

MC destruction occurs via reaction with reactive radicals and ions (Si<sup>•</sup>, Si-O<sup>•</sup>...) on the fresh surfaces of soil particles. MC treatment produces a multitude of reactive sites with destruction reactions occurring rapidly on contact between organic molecules and reactive sites. This is generally a solid-solid reaction limited by the migration of reactants toward each other. MC processing accelerates these solid-solid reactions by repeatedly bringing reactants into intimate contact with each other, by giving a constant supply of reactive sites and by removing reaction products. Even so solid-solid reactions are typically much slower than gas-solid reactions where mobile gaseous reactants quickly migrate to reactive sites. If volatilized, a PCB molecule will quickly react with the reactive radicals and ions on the fresh mineral surfaces to form the amorphous carbon and inorganic chloride final products.

While the pilot MCD™ reactor used in the TS is not a totally closed system, it has been designed to operate as an essentially closed system with soil input and output ports either sealed mechanically or blocked with soil during feed and discharge events. Hence this restricts to a minimum the flow of gases into and out of the MCD™ reactor. Without the release or flow of gases the volatilization of PCBs will be restricted.

The vastly increased ratio of Arochlors 1248/1254 to Arochlor 1260 after MCD™ treatment mentioned above is evidence of mechanochemical destruction over volatilization, as simple volatilization will not result in the formation of less chlorinated PCBs. Also lesser chlorinated Arochlor 1248/1254 PCBs are more volatile than heavier Arochlor 1260 PCBs so the ratio should trend the other way based on a volatilization mechanism.

Based on the discussion above, the risk of significant release of volatilized PCB from the MCD™ reactor is low. Gas sampling of MCD™ reactor inlet and outlet augers for PCBs during a 'proof of performance' period at the start of a full scale MCD™ remediation of the PCB Hotspot stockpiles at HPS would be prudent. Such a strategy was employed during the proof of



performance trial of the full scale MCD™ plant at Mapua where gaseous emissions were within regulatory limits for DDT (and metabolites), dioxins/furans and PCBs (Thiess Services Ltd, 2004).

### 7.2.9. Dioxins

The risk of dioxin formation and release during MCD™ treatment of HPS soils is considered to be low. Discussed below are arguments to support this conclusion based on research performed by EDL and others.

The first mechanism insuring that dioxins are not formed are the reducing conditions inside the MCD™ reactor. During MCD™ treatment of organics, the carbon and hydrogen in the organic compounds in the soil react rapidly with atmospheric oxygen (O<sub>2</sub>) to give carbon dioxide (CO<sub>2</sub>). The molar ratio of carbon and hydrogen to O<sub>2</sub> in the soil entering the MCD™ reactor during continuous full scale operation is generally greater than 100 to 1. Therefore oxygen will be rapidly and quantitatively consumed and reducing conditions will prevail effectively preventing dioxin formation. Oxygen atoms contained in the inorganic soil minerals can oxidize carbon to CO<sub>2</sub> according to the literature (Heineke, 1984; Lin & Nativ, 1979; Tkacova, 1989; Gaffet et al., 1999; Gilman, 1996) however in research under an inert nitrogen atmosphere oxygenated organic products were not detected indicating that oxygen in soil minerals and water is not available for reaction with organic compounds (EDL, unpublished research).

Every organic compound, without exception, mechanochemically treated by EDL has been destroyed. MC destruction in quartz occurs with methane, PCBs, DDT, DDD, DDE, PAHs, hydrocarbons, dieldrin, PCP, HCB to name but a few compounds. Dioxins are organic compounds similar in chemical structure and properties to several of the compounds above and hence there is strong evidence to suggest that they too will be susceptible to MC destruction. Indeed, dioxins have been mechanochemically destroyed in quartz sand in research by published by Kaupp et al. (2003). Hence the full range of dioxins and furans will also be susceptible to MCD™.

Based on the discussion regarding intermediates above, if intermediate dioxins are formed it will be at very low concentrations with the maximum yield of <1% of the original PCB concentration. Given the reducing conditions prevailing in the MCD™ reactor as explained above, and the lack of oxygenated products in the absence of oxygen, the maximum yield will be considerably less and any dioxin intermediates formed will be destroyed as MCD™ treatment progresses. Hence the risk of dioxin formation and release is low. Confirmation of the absence of dioxins can be



checked via sampling of solids and gases exiting the MCD™ reactor during a full scale 'proof of performance' period. The appropriate use of activated carbon filters will give added safety against emission of volatilized PCBs and dioxins during full scale remediation if considered necessary.

### 7.3. Stage 2 – Stabilization of Metals

Comparison of the baseline and MCD™ treated samples indicates that the drying and MCD™ treatment processes do not result in a significant change in concentration of individual metals. The only possible exception is mercury which is reduced in concentration from 6.3 mg/kg to <0.13 mg/kg. Mercury is a volatile metal and hence drying and MCD™ treatment do have the potential to volatilize this element. The reduction in mercury concentration is consistent across all four soil samples analyzed and hence is reasonably conclusive evidence that volatilization of mercury does occur during MCD™ treatment. This will be an issue during MCD™ treatment of soils containing high concentrations of mercury. Baseline sampling and analysis of HPS PCB Stockpile soils indicates that mercury concentrations are low (<10 mg/kg).

The low TCLP results in the MCD™ treated samples (pre-stabilization) are interesting with all results below the SAC for the metals present. This effectively makes the stabilization process with addition of Apatite II™ largely redundant. PIMS relies on metals and phosphate dissolving into water where precipitation reactions occur through the formation of metal phosphates. If little metal dissolves, as would be the case in these samples based on the MCD™ treated TCLP results, then there will not be many stabilization reactions.

While the positive TCLP results in the MCD™ treated samples are encouraging, they are not altogether surprising. The proprietary reagents added during MCD™ treatment breakdown inside the MCD™ reactor. A number of the breakdown products are chemically similar to common stabilization agents. Hence during MC treatment these reagent breakdown products will react with metals to form low solubility products. There are also numerous reports in the literature regarding the interaction of inorganic compounds and elements during MC treatment. The formation of metal silicates which tend to have low solubility is common (Urakaev, 2003; Lin & Nativ, 1979; Lioa & Senna, 1992; Heineke, 1984; Avvakumov et al., 1994). Phase transformation also occurs which can reduce solubility considerably, such as occurs in the transformation of calcite to aragonite (Fernandez-Bertran, 1999; Lin & Nativ, 1979). A range of



other inorganic reactions are also possible (Lin & Nadiy, 1979; Tkacova, 1989; Heineke, 1984; Gaffet et al., 1999).

The STLC results shown in Figure 10 are generally higher than the TCLP results in Figure 9. This reflects the difference in the extraction procedures used for the two methods with STLC using citric acid (strong) and 48 hours extraction compared to acetic acid (weak) and 18 hours extraction for TCLP. The STLC is part of the California regulations on disposal of wastes to landfills and the TCLP is a Federal (EPA) threshold. The STLC result for Pb is above the SAC of <5 mg/l for several samples analyzed. The stabilization of metals to the more stringent STLC standard should not present an impossible hurdle however with many successful stabilization processes well proven. Modification of the metal stabilization treatment should therefore yield soil meeting the SAC.

It should also be noted that the addition of sufficient water to the contaminated soil and Apatite II™ during stabilization treatment is critical with stabilization reactions occurring in the aqueous phase (Wright et al., 2004). Unfortunately this may not have been the case during the TS, with the desire to produce a final remediated soil product with good geotechnical properties limiting the amount of water added during stabilization treatment.

The two metals in highest concentration in TS samples, Cu and Pb, both show significant reductions in concentration due to the stabilizing effect of MCD™ and/or Apatite II™ treatment. Zinc shows some reduction in TCLP but the STLC results are less conclusive. Other metals are present in low concentrations are leaching trends on MCD™ and stabilization treatment are less obvious.

#### **7.4. Full Scale MCD™ Modeling**

The pilot Series III MCD™ reactor to be used in the TS is a scaled down replica of the full scale Series III MCD™ reactor. The grinding action in the pilot reactor is identical to that of the full scale reactor, making the mathematical modeling of the full scale MCD™ reactor reasonably straightforward. A macro-kinetic MCD™ model has been developed to predict full scale reactor performance based on a global MC model proposed by Delogu et al. (2003) and 1<sup>st</sup> order reaction kinetics. The global MC model accurately calculates the mechanical energy intensity, a key parameter in mechanochemically initiated reactions. The influence of other important parameters such as soil mineral composition, addition of reagents, soil moisture, MCD™ reactor temperature and MCD™ reactor atmosphere, must also be accounted for. Research has shown that 1<sup>st</sup> order



reaction kinetics apply to the MC destruction of organic compounds such as PCBs. Hence mechanical energy intensity and the other parameters mentioned above can be used to calculate the rate constant (k) for the change in concentration of PCBs as they are mechanochemically destroyed. The mathematical model is described below.

The mechanical energy intensity, I, is defined as

$$I = N E = \frac{1}{2} N m_b v_b^2 \quad \text{Equation 1.}$$

where N is the collision frequency, E is the mechanical (or kinetic) energy, and  $m_b$  and  $v_b$  are the ball mass and ball velocity respectively

Referred to the MCD™ reactor charge,  $m_p$ , I becomes

$$I_m = I / m_p = N E / m_p \quad \text{Equation 2.}$$

In the MCD™ process, destruction of organic compounds appears to follow first order kinetics. Therefore the concentration of contaminant X at any given time is defined as

$$[X] = [X]_0 e^{-kt} \quad \text{Equation 3.}$$

where  $[X]_0$  is the initial concentration of X and k is the rate constant for the destruction process proportional to mechanical energy intensity  $I_m$ , soil mineral composition and moisture content, reagent type and addition rate, concentration of atmospheric oxygen, MCD™ reactor temperature and the free space inside the MCD™ reactor for ball/soil movement.

The nine soil samples selected for the TS by the Navy are deemed to be representative of the range of soil compositions and contamination levels in PCB Hotspot Stockpiles 5, 6 and 7. Assuming that the soil moisture, the reagent type and amount, the O<sub>2</sub> content, temperature and free space in the MCD™ reactor remain the same, then rate constant k will only be influenced by mechanical energy intensity (EDL, unpublished research). Mechanical energy intensity is dependent on the collision frequency, and the mass and velocity of the grinding balls. Scaling up from the pilot to the full scale MCD™ reactor gives a 6 fold increase in mechanical energy intensity.

The lack of PCB concentration results at sampling times between 0 and 15 minutes, where, based on pseudo-first order kinetics, the PCB concentrations will be higher, makes it difficult to calculate the first order rate constant. Either the untreated and 15 minute results are used, which gives only two data points, or the longer milling times are included, predicting a far higher PCB concentration at 15 minutes than is obtained by analysis of the 15 minute samples. Neither



approach is particularly satisfactory from a scientific point of view. However given that during the TS, the pilot MCD™ reactor successfully treated 8 separate 25 kg samples of contaminated soil to below the 1,000 µg/kg SAC within 15 minutes, we can be confident that this is a reasonable reflection of reality. Hence a production rate of 100 kg/hr through the pilot MCD™ reactor should be possible. With a 6 fold increase in mechanical energy intensity, the destruction time needed in the full scale MCD™ reactor will be in the order of 2 ½ minutes. This gives an estimated production rate of 600 kg/hr for each reactor tube. With each full scale MCD™ reactor unit containing 5 individual MCD™ reactor tubes, the full scale MCD™ reactor unit throughput is estimated to be 3 t/hr. Based on an operational availability of 40 hours per week, two MCD™ reactor units and 10,000 tonne of contaminated soil, it will take just over 40 weeks to remediate PCB Hotspot Stockpiles 5, 6 and 7.



## **8.0 CONCLUSIONS AND RECOMMENDATIONS**

The TS conducted at HPS successfully evaluated the MCD™ and post-MCD™ metal stabilization processes for remediation of PCB and metal contaminants observed in PCB Hotspot Stockpiles 5, 6 and 7. The following conclusions are based on an evaluation of the results of Stage 1 MCD™ treatment and the Stage 2 metal stabilization undertaken during the TS.

### **8.1. Conclusions Stage 1 – MCD™ Treatment**

The MCD™ technology successfully achieved remediation to below the SAC (1,000 µg/kg), reducing PCB concentration in several samples to non-detectable levels (<15 µg/kg) and achieving destruction efficiencies >98%. The detection of Arochlor 1248 and 1254 PCBs in the MCD™ treated samples at similar concentrations to Arochlor 1260 PCBs is expected as dechlorination is one of several mechanisms by which MC destruction occurs.

Remediation of OCPs (DDT and dieldrin) by the MCD™ technology in TS soil samples achieved reduction of detected OCP concentration to non-detectable levels (<17 µg/kg) and destruction efficiencies >99%.

According to the literature, PCBs and OCPs are converted into a high molecular weight amorphous carbon product and inorganic chloride on MC treatment. This carbon product then goes on to form other carbon species not detectable by TOC analysis (CO<sub>2</sub>, carbonates, and other species). Inorganic chloride, from the PCBs and already present in the soil, binds to the inorganic soil matrix and hence is not easily extractable in soluble chloride analyses. Volatilization of PCBs inside the MCD™ reactor is likely given the conversion of mechanical energy to heat during MC treatment. These volatilized PCBs will quickly undergo MC destruction and good sealing of the MCD™ reactor will minimize release of vapor phase PCBs. Based on published and unpublished research, the risk of formation and release of dioxins is low. Gas sampling and analysis for PCBs and dioxins should be conducted during further pilot or full scale trials to confirm the conclusions above, which are based on previous research.

### **8.2. Conclusions Stage 2- Metal Stabilization**

Stabilization of metals occurred during MCD™ treatment giving a mean TCLP result for Pb of 0.55 mg/l, comfortably below the SAC of 5 mg/l. The TCLP results for other metals were also very low and well below SAC levels for each. STLC results were higher with Pb exceeding the



SAC. The stabilization treatment with Apatite II™ was largely ineffective due to the low TCLP concentrations in MCD™ treated samples and may have been affected by the limited water addition during stabilization. The use of alternative stabilizing agents such as lime/cement may yield superior results.

### **8.3. Recommendations**

The TS demonstrates the potential for the use of a full scale MCD™ plant at HPS for the remediation of PCBs. Appropriate modification of the metal stabilizing treatment should yield TCLP and STLC leaching results below regulatory limits for metals. Hence remediation to below the SAC (1,000 µg/kg PCBs and 5 mg/l TCLP Pb) can be achieved, allowing reinstatement of soil on site at any depth. Resolution of the volatilization issue to the satisfaction of all parties should be given priority. This can be effectively addressed by gas sampling and analysis during a further pilot TS or during a 'Proof of Performance' phase at the start of the full scale remediation. Discussion between Shaw, EDL, Navy and other relevant groups should proceed to determine the way forward to further evaluate the ability of the MCD™ technology for the remediation of PCBs in HPS soils.



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## 10.0. Photos



Drying and Screening of PCB Hotspot Stockpile Soil Samples



Arrival and setting up of the Pilot Series III MCD™ Reactor  
Building 414, Hunters Point Shipyard, San Francisco.



Mixing of reagents and preparation of soil samples for MCD™ treatment (1)



Mixing of reagents and preparation of soil samples for MCD™ treatment (2)



Loading of MCD™ Reactor in Building 414



Metal Stabilization treatment



*Appendix A*

*Soil Analyses Data Summary Table*

Please refer to the enclosed CD Media for all related documentation

APPENDIX A – SOIL ANALYSES DATA SUMMARY TABLE,  
IS CONTAINED ON ELECTRONIC MEDIA AND IS TOO  
VOLUMINOUS TO PRINT.

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