MECHANOCHEMICAL DESTRUCTION OF PCBS AT HUNTERS POINT SHIPYARD FOR THE US NAVY

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ABSTRACT: Environmental Decontamination Ltd (EDL), a New Zealand owned company based in Auckland, have continued to develop their MechanoChemical Destruction (MCD™) remediation technology following the successful remediation of the Fruitgrowers Chemical Company site at Mapua. This paper summarises the progress made since Mapua, focussing on trials conducted with Shaw Environmental Inc. (Shaw) for the US Navy at Hunters Point Shipyard (HPS) near downtown San Francisco. The HPS naval base contains areas of land contaminated with PCBs and heavy metals, the result of historic naval and civilian activities, which must be remediated prior to base closure. EDL and Shaw have successfully completed two sets of trials using the MCD™ technology to remediate contaminated soil at HPS. PCB destruction efficiencies up to 99.99% have been achieved and residual PCB levels were reduced to <1mg/kg. Dioxins and furans, several organochlorine pesticides (OCPs) and total petroleum hydrocarbons (TPHs), present in the soil as co-contaminants, were also mechanochemically destroyed. Extensive gas sampling confirmed that volatilization and release of PCBs, dioxins, furans and OCPs during MCD™ treatment was negligible. Following MCD™ treatment, soil was stabilized to minimize leaching of metal contaminants such as lead, copper and chromium. These trials have confirmed the efficacy of the MCD technology in remediation of PCBs in HPS soils and will allow remediation and reinstatement on site rather than disposal to a hazardous waste landfill.

INTRODUCTION

Mechanochemistry, using mechanical energy to initiate chemical reactions, has been exploited for centuries but began to increase in prominence in the 1980s and 1990s (Heineke, 1984). The use of mechanochemistry for the destruction of toxic organic compounds was first investigated by researchers at the University of Western Australia who found that DDT and other toxic organic compounds could be broken down into a carbon residue and inorganic chloride by milling in the presence of calcium oxide (Rowlands et al., 1994; Hall et al., 1996). More recently quartz sand has been used successfully in the mechanochemical destruction of polycyclic aromatic hydrocarbons (PAHs) and dioxins (Field et al., 1997; Kaupp et al., 2002). Milling of quartz results in the cleavage of silicon - oxygen (Si-O) bonds to form so called E’ centre and non-bridging oxygen hole centre radicals which react with organic molecules breaking them down into a carbon matrix and, in the case of organochlorines, inorganic chloride (Kaupp et al., 2002). Mechanochemical reactions are complex and a range of mechanisms can be involved (Heineke, 1984), although it is understood that reactions are initiated by free radicals formed during fracture of silicate-rich soil particles. Mechanochemical destruction of a wide variety of toxic organic compounds has been achieved in quartz sand and real contaminated soils in research at Auckland University of Technology (Bellingham, 2006).
Following on from the remediation of the Fruitgrowers Chemical Company site in Mapua, where DDT concentrations over 3,000 mg/kg were successfully reduced to below 200 mg/kg, Environmental Decontamination Ltd. (EDL) has continued to optimise the MechanoChemical Destruction (MCD™) technology. The result is the purpose built Series V MCD™ reactor used by EDL and Shaw Environmental, Inc. (Shaw) in an MCD™ treatability study for the U.S. Navy at Hunters Point Shipyard (HPS) in San Francisco. HPS soils have been impacted by PCBs and lead due to historic naval and civilian operations at the site. Closure of HPS includes conducting environmental remediation activities and transfer of the property to the City of San Francisco for future civilian use.

PCB concentrations >300 mg/kg have been detected in PCB Hot Spot Stockpiles on site. The initial treatability study in 2006 using contaminated soil containing up to 100 mg/kg PCBs found that the MCD™ technology was able to effectively reduce PCB concentrations in soil to the treatment goal of <1 mg/kg. However, doubt remained about possible volatilization of PCBs and other contaminants. Hence, a Supplementary Treatability Study (STS) was designed to provide the data needed to resolve these concerns.

MATERIALS AND METHODS

Soil for use in the STS was collected from PCB Hot Spot Stockpiles 12 and 15, dried in an incubator set at 55 degrees Celsius for 24 hours, and sieved to remove particle size fraction greater than 20 mm. The soil was then divided into 20 kg batches for use in the STS. Each batch of soil was sampled immediately prior to MCD™ treatment. No volatile organic compounds (VOCs) were detected in the air with handheld photoionization and dust detectors during drying and sieving operations.

The Series V MCD™ reactor, a purpose built high energy ball mill, was warmed up for 30 minutes prior to the start of each trial. The contaminated soil (20kg) was loaded into the MCD™ reactor along with quartz sand (5% by wt) and selected proprietary reagents (1% by wt). An MCD™ treatment time of 15 minutes was selected for batches 1 through 7 based on the results of the previous treatability study where 15 minutes was sufficient to reduce PCB concentrations to below the 1 mg/kg target. This treatment time proved to be inadequate due to higher than anticipated PCB concentrations, coupled with high diesel and motor oil hydrocarbon concentrations which compete for reaction sites on the new quartz surfaces. Hence a second round of trials were performed on batches 8 through 10, and batch 12, which received 60 and 30 minutes of MCD™ treatment, respectively.

The Series V MCD™ pilot reactor is a closed batch system. Entry and exit valves for soil are closed during normal operation. However, heat resulting from mechanical work in the reactor causes the pressure in the reactor drum to increase. Under normal operation this pressure is released via a poppet valve through an activated carbon filter. For batches 1 through 7 off-gas sampling was performed to evaluate the potential volatilization of contaminants of concern.
The pressure relief valve on the MCD™ reactor was kept closed, and off-gases were released manually to keep reactor pressure below 5 psig. Off-gases were sent to the sampling trains and make-up air was used to provide a steady gas flow through the sampling trains. During manual pressure release events the reactor off-gas replaced the air, with the total flow rate remaining constant. At the conclusion of each 15 minute trial, the air supply to the off-gas sampling train was stopped and the MCD™ reactor purged with nitrogen for approximately 20 minutes to give a purge volume four times greater than the reactor headspace volume. Separate off-gas sampling traps were used and analyzed for PCBs (EPA Method 1668A), dioxins and furans (EPA Method 23/8290), pesticides (EPA Method TO-4A), and hydrochloric acid/chlorine (EPA Method 300.0). A sample of the off-gas was also collected directly from the reactor to a Summa canister. The major components of the off-gas sampling train are shown in Figure 1 below.

For batch 7, the granular activated carbon (GAC) filter was attached to the reactor's off-gas vent. During the run and during the reactor headspace purge, off-gas was sampled from before and after the GAC filter. Sampling trains were as shown in Figure 1 above.
At the conclusion of MCD™ treatment and following the nitrogen purge of the reactor headspace the soil was discharged from the MCD™ reactor and weighed. Samples of treated soil were taken and analyzed for PCBs (EPA Methods 8082 & 1668A), dioxins and furans (EPA Method 8290), OCPs (EPA Method 8081A), TPH (EPA Method 5035/8015B), SVOCs (EPA Method 8270C), VOCs (EPA Method 5035/8260B) and Total Organic Chloride (EPA Method 9020B). Inorganic chloride in the MCD™ treated soils were analyzed using standard extractable chloride and alkali fusion methods and ion chromatography (EPA Method 9056). Total chlorides were analyzed using X-ray fluorescence (XRF).

Stabilization is a simple procedure where soil, selected reagents, and water are well mixed and allowed to cure for a minimum of 24 hours prior to analysis. The post-MCD™ soil was combined, homogenized and sampled, prior to the addition of Portland cement at 15%, 20% and 25% by weight. Sufficient water was added to the soil/Portland cement mix to give it the moisture level and texture typical of damp garden soil. The stabilization aliquots were sufficiently small that mixing could be performed by hand. Following stabilization, samples were taken and analysed for heavy metals using the Soluble Threshold Limit Concentration (STLC) procedure (CCR Title 22 - WET) and Toxicity Characteristic Leaching Procedure (TCLP, EPA Methods 1311/6010B/7470A). Pre-stabilization samples were analyzed using the STLC and TCLP procedures, and total metal concentrations were determined using EPA Method 6010B. Triple super phosphate and ferrous sulphate, both at 2% by weight, were added to the soil samples treated for 30 and 60 minutes in the MCD™ reactor to stabilize copper and chromium which exceeded STLC limits when Portland cement alone was used.

RESULTS AND DISCUSSION

PCBs. In analysis using the Aroclor pattern matching technique, only Aroclor 1260 was detected in Pre- and Post-MCD™ samples. The averaged results for the six 15 minute, one 30 minute, and three 60 minute batches are presented below in Figure 1. The Aroclor results (EPA Method 8082) for the six 15 minute runs are consistent with individual PCB congener results (EPA Method 1668A). Both methods of analysis indicated a destruction efficiency (DE) of approximately 72% for total PCBs. Hence, while a significant proportion of the PCBs were destroyed, the residual PCB concentrations remained above the 1 mg/kg guideline.

The 15 minute MCD™ treatment time was based on the results from the original treatability study which used soil from PCB Hot Spot Stockpiles 5, 6 and 7. The concentration of PCBs in untreated soil used in the original trials in 2006 was generally <100 mg/kg compared to between 250 and 300 mg/kg in the soil used in this study. Hence, with higher starting PCB concentrations a longer MCD™ treatment time is expected. The TPH concentration, predominantly in the diesel and motor oil ranges, in the untreated soil was also very high in the soil used in this study. The indiscriminate nature of the MCD™ process with respect to the destruction of organic compounds means that TPHs competed directly with PCBs for reaction at active sites generated by grinding of quartz sand and soil minerals. Therefore high concentrations of TPH and other organics can reduce the destruction rate for the target contaminants, in this case PCBs.
The results for the 30 and 60 minute batches show excellent destruction of PCBs, with residual PCBs in the treated soil <0.025 mg/kg in all samples. The DE achieved was >99.99% and treated soils were comfortably below the 1 mg/kg criteria for hazardous waste and the 0.22 mg/kg criteria for residential soils under EPA Region 9 risk-based preliminary remediation goal (PRG).

![FIGURE 2. Mechanochemical destruction of PCBs for 15, 30 and 60 minute MCD™ treatment times.](image)

During the 15-minute runs, the off-gas from the reactor was sampled for PCBs and analyzed by the PCB congener method (1668A). The results showed that the off-gas contained a negligible amount of PCBs, equivalent to less than 0.006% of the mass of PCBs destroyed. Hence volatilization is not a significant mechanism for PCB removal from the soil during MCD™ treatment.

The sampling of the off-gas and GAC for batch 7 was intended to quantify possible loading of PCBs on the carbon filter. Samples of the carbon were taken from the inlet, middle, and outlet portions of the carbon bed. Samples of the off-gas were taken from the off-gas streams before and after the GAC filter. Total PCB concentrations were measured for these samples using the Aroclor pattern matching method. All results for these samples were non-detect at approximately 10 µg/kg for the carbon and 10 µg/sample for the off-gas samples.

The PCB congener analyses for the 15-minute batches show that the DE of the more chlorinated PCBs was higher than for the lower chlorinated PCBs. The results also show that some mono-, di- and tri-chlorinated PCBs are formed although the amount is negligible compared to total mass of PCBs destroyed. Hence dechlorination is at best only a minor pathway for the destruction of PCBs where the ultimate fate is conversion into an amorphous carbon residue and inorganic chloride according to other research (Bellingham, 2006; Kaupp et al., 2002). The VOC and SVOC results from soil and off-gas samples indicate that this
conversion occurs without the generation of significant quantities of chlorinated organic intermediate products. This observation is consistent with other research (Bellingham, 2006).

**Dioxins and Furans.** The averaged results for the 15 and 60 minute batches are presented in Table 1 below. The increase in dioxin total toxic equivalents (TEQ) in the 15 minute trials is due almost entirely to the oxidation of PCB molecules to form furans, a relatively simple chemical reaction. However, the results show that when MCD™ treatment is continued and the residual PCB concentration falls below the 1 mg/kg target, the residual dioxin and furan concentration is also very low.

**TABLE 1. Mechanochemical destruction of dioxins and furans for 15 and 60 minute MCD™ treatment times.**

<table>
<thead>
<tr>
<th></th>
<th>Pre-MCD (ng/kg)</th>
<th>Post-MCD (ng/kg)</th>
<th>Destruction Efficiency</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>TEQ Total</td>
<td>TEQ Total</td>
<td>TEQ Total</td>
</tr>
<tr>
<td>15 min samples</td>
<td>184 - N/A</td>
<td>1,200 -</td>
<td>N/A 94%</td>
</tr>
<tr>
<td>60 min samples</td>
<td>265 14,400</td>
<td>15.5 319</td>
<td>98%</td>
</tr>
</tbody>
</table>

During the 15-minute runs the off-gas from the reactor was sampled and analyzed for dioxins and furans. The mass of dioxins and furans detected in the off-gas is less than 0.005% of the starting concentration on a TEQ basis. This confirms that although a limited amount of dioxins and furans were formed during the 15-minute runs, they essentially remain in the soil and are not released in the off-gas. This ultimately allows for a significant reduction in dioxin and furan concentrations in the soil when MCD™ treatment is allowed to proceed to completion as shown in the 60-minute trials.

The slightly higher DE for total dioxins compared to TEQ dioxins indicates that some dechlorination may have taken place. This can be of concern due to the formation of more toxic tetra and penta dioxins from less toxic hexa, hepta and octa dioxins. As with PCBs however dechlorination is only a minor pathway and overall there is significant reduction for tetra and penta dioxins as well as higher chlorinated dioxins.

**Organochlorine Pesticides.** Several OCPs, namely DDT, dieldrin, endrin, methoxychlor, and heptachlor epoxide, were detected in the untreated soil. Significant destruction (72%) of OCPs occurred during the 15-minute trials rising to >99.9% in the 30 and 60 minute trials where all OCPs were below detection limits (µg/kg level). The average mass of OCPs detected in the off-gas equated to less than 0.1% of the total amount of OCPs present in the pre-MCD™ soils. Hence, as with PCBs, the loss of OCPs through volatilization was negligible.

**Total Petroleum Hydrocarbon.** TPH in the diesel and motor oil ranges was present in very high concentrations in the untreated soil (approximately an order of magnitude greater than
PCBs). The TPH results are consistent across the 15 minute trials with average pre- and post-MCD™ concentrations of 1,995 and 518 mg/kg respectively. The average DE for the 15 minute trials was 74%, similar to that achieved for PCBs during the same trials. The off-gas was not analyzed for TPH but the VOC and SVOC samples did indicate the presence of minor amounts of hydrocarbons and light hydrocarbon gases. TPH analysis was not performed for 30 and 60 minute trials.

**Chloride.** During the mecanochemical treatment of PCBs, the chloride associated with the PCB molecules is removed and inorganic chloride compounds are formed with metals in the soil. Hence an increase in soluble chloride is expected as organic chloride associated with the PCBs is transformed to inorganic chloride. The TOX result showed that chlorinated organic compounds were removed from the soil. This was not the case with both extraction and fusion analyses however, which indicated a reduction in soluble chloride following MCD™ treatment. This phenomenon is understood to be a result of trapping of chloride ions in pores, cracks, dislocations and grain boundaries of the soil particles which have undergone intense mechanical deformation. In research involving the mecanochemical treatment of DDT in quartz sand where the yield of soluble chloride reduced as mecanochemical treatment progressed, XRF analysis indicated that the total chloride concentration stayed constant (Bellingham, 2006).

As with the water extraction and alkali fusion chloride results above, the chloride content determined by XRF in Post-MCD™ samples was significantly lower than in Pre-MCD™ samples. The difference was approximately 0.05 to 0.06%, or 500 to 600 mg/kg. This is significantly more than the amount of chloride contained in the PCB molecules in Pre-MCD™ soils (~180 mg/kg for 300 mg/kg Aroclor 1260). Interestingly, the XRF results also indicate that Al₂O₃, CaO and S concentrations are all significantly lower in the Post-MCD™ samples than in the Pre-MCD™ samples. A small reduction is expected with the addition of 5% quartz sand and 1% proprietary reagents to the soil during MCD™ treatment, but this dilution does not account for the 20 to 65% reduction in Al₂O₃, CaO and S concentrations observed. These results suggest that there is some sort of interference complicating the analysis by XRF. Resolution of the chloride mass balance is an important area for ongoing research.

**Stabilization of Metals.** The lead concentration in the pre-stabilization composite was 120 mg/kg compared to over 1000 mg/kg in the soil samples used in the original treatability study. While TCLP results for all metals were below guideline levels in pre- and post-stabilization samples, the pre-stabilization STLC result was 5.2 mg/L, and hence lead stabilization was required for the MCD™ treated soil in order to meet the 5 mg/L STLC concentration applicable in Califórnia. Treatment with Portland cement at 15%, 20% and 25% by weight resulted in STLC results more than an order of magnitude below the guideline. However the use of copper in the proprietary reagents, combined with the high pH resulting from the cement stabilization, resulted in high STLC results for copper. Also, the use of high chrome (23% chromium) components in the MCD™ reactor gave elevated STLC results for chromium in the samples subjected to 30 and 60 minutes of MCD™ treatment. High copper and chromium levels were successfully reduced to below guideline levels by the addition of triple super phosphate (2% by weight) and ferrous sulphate (2% by weight), respectively. Research has shown that the influence of copper on PCB destruction is minor if other
parameters such as milling intensity and quartz content of the soil are optimised. Hence the use of copper as a reagent will be phased out. A change to lower chromium content (2%) MCD™ reactor components and optimization of MCD™ treatment time should resolve the chromium issues. Hence lower stabilization reagent addition rates should be achievable during full scale remediation.

CONCLUSIONS

The MCD™ technology successfully reduced PCB concentrations from >250 mg/kg to <1 mg/kg when the appropriate treatment time was applied. Destruction efficiencies greater than 99.99% were achieved. Dioxins and furans, several OCPs and TPH, present in the untreated soils as co-contaminants, were also mechanochemically destroyed. Gas sampling confirmed that volatilization of PCBs, dioxins, furans and OCPs was negligible. The ultimate fate of the organic compounds, based on other research (Bellingham, 2006; Kaupp et al., 2002), is conversion to a carbon residue and inorganic chloride. Further research is needed to complete the chloride mass balance however due to analytical interferences. MCD™ treated soil was stabilized with Portland cement to minimize leaching of metal contaminants such as lead. The STS confirmed that MCD™ treatment followed by metal stabilization can successfully remediate PCB and lead contaminated Hunters Point Shipyard soil, allowing for reinstatement on site rather than disposal to a hazardous waste landfill.

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