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Remediation of Dioxin, Pentachlorophenol and Organochlorine Pesticide Contaminated Soils

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Abstract

The remediation of dioxin (polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF)), pentachlorophenol (PCP) and organochlorine pesticide contaminated soil using indirect thermal desorption and chemical destruction has been successfully developed and demonstrated in a phased programme. Bench scale laboratory studies have identified the conditions and additives required to treat soils contaminated with these organochlorine contaminants. Soil with initial PCP levels of 2900 mg/kg and initial dioxin levels of 75 µgTEQ/kg were reduced to less than 0.01 mg/kg and to 0.08 µgTEQ/kg respectively.

These parameters have been successfully scaled up and transferred to a continuous pilot plant, processing 40 - 80 kg soil per hour. PCP in the soils was reduced from initial levels of 561 - 1440 mg/kg to less than 0.02 mg/kg. Dioxins in the soil were reduced from 17-18 µgTEQ/kg to less than the target of 1 µgTEQ/kg, and in many cases less than 0.2 µgTEQ/kg. In another series of trials, PCP and dioxin contaminated sawdust was mixed with soil and sand at 10% and 25% levels. PCP in the mixtures was reduced from initial levels of 2020 - 3110 mg/kg to less than 0.02 mg/kg and dioxins from initial levels of 190 - 245 µgTEQ/kg to 1.2 - 3.2 µgTEQ/kg. A further set of trials treated the collected dusts from the previous trials. The matrix, when the dusts were mixed with sand, had initial dioxin levels of 1280 µgTEQ/kg. Treatment in the process resulted in final levels of less than 0.08 µgTEQ/kg.

Soils containing the organochlorine pesticides DDT (482 mg/kg), lindane (γ -HCH) (241 mg/kg), and chlorothalonil (587 mg/kg) respectively, after treatment in the process resulted in levels of less than 0.001 mg/kg for DDT and lindane and less than 0.1 mg/kg for chlorothalonil.

Design of a 5 tonne/hr indirectly heated thermal desorption plant has been made with the dust and sludge arising from the emission control processes being recycled to effect a single stage treatment plant which can treat a range of soils contaminated with various levels of PCP, dioxins and organochlorine pesticides.

Introduction

There are a number of small and medium sized sites in New Zealand that have residual contamination from the past use of persistent organochlorine compounds. These compounds include organochlorine pesticides such as DDT and lindane, and pentachlorophenol (PCP) and its

salts. The pesticide sites include the site of a now disused pesticide manufacturing and formulation plant. This site also has off-site contamination of sediments in a local estuary.

PCP was used either in water based solutions as anti-sap stain reagents or in heavy oil solutions as timber preservatives. Soils and structures on these sites have been contaminated to varying degrees by PCP and its dioxin, particularly octachlorodibenzo-p-dioxin (OCDD), co-contaminants. In a two phase programme of soil treatability we have demonstrated the effectiveness of an indirectly heated soil thermal desorption process. Phase 1 was a small scale batch study conducted in the laboratory and phase 2 was a continuous process pilot plant scale study. These studies were designed to not only effect the removal of the contaminants from the soil but also to facilitate the in situ destruction of the contaminants by chemical reaction. The target levels for the process were the Interim Residential Soil Acceptance Criteria in New Zealand of 0.05 mg/kg for PCP and 1.5 µgTEQ/kg for dioxins.

This paper reports the results of these studies, and in particular focuses on the results of phase 2, the pilot plant study.

Experimental

Phase 1. Laboratory Study.

The laboratory thermal desorption trials were conducted in two types of equipment. Most were conducted in a stainless steel reactor (Parr 4560) modified to operate at atmospheric pressure under an atmosphere of nitrogen. The reactor was attached to a trap system comprising an ice/salt cooled (-20°C) trap, an ambient temperature condensate trap and two activated carbon traps. An anchor paddle was used to slowly stir the soil. The reactor could be rapidly heated to 350°C. The final trials were conducted in a specially constructed glass barrel thermal desorber that mimics continuous processing by slowly rotating the soil, while rapidly heating to temperatures of 450°C. This also was able to be operated under an inert atmosphere and was connected to a trap system.

Experiments were conducted using 100g of ~ 1mm sieved soil, mixed with any additives. After charging the reactor with the soil mixture, and purging with nitrogen, the soil was rapidly heated to temperature for set time periods, then rapidly cooled. Samples were carefully obtained and the equipment thoroughly cleaned prior to the next trial.

Parameters examined included time, temperature, water content, alkali additive, catalyst additive and accelerant additive. This paper presents the results of a selection of the trials conducted in this phase of the investigation.

Phase 2. Pilot Plant Study.

The continuous, indirectly heated thermal treatment pilot plant comprised a mixing and feed section, a process section with external electrical heaters and twin hollow shafts fitted with paddles to provide intense mixing and conveying, heated by hot oil flowing inside them. Soil flow through the system was controlled by a combination of feed rate and screw speed of the shafts. Treated soil was collected in an exit section into enclosed clean 220 litre steel drums. The plant was operated under a stream of nitrogen and the off gases passed through a drop out drum to collect larger dust

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particles, then through a wet scrubber section to cool and collect solids and condensates and finally through primary and secondary activated carbon cartridges prior to venting to atmosphere. A suction fan was placed after the carbon cartridges to maintain a negative pressure in the equipment during the treatment process.

Trials were conducted using soil sieved to <10mm and dried to <10% moisture. An alkaline earth oxide additive was added to the soil at a rate of 10%. Flow rates of 40, 60 and 80 kg/hour and temperatures of 450°C were employed.

In addition to PCP and dioxin contaminated soils from three sites, matrices comprising soil (90%) and PCP contaminated sawdust (10%); sand (75%) and PCP contaminated sawdust (25%); sand with DDT and lindane; and sand mixed with the combined drop out dusts were also treated. One of the PCP and dioxin contaminated soils was also contaminated with the organochlorine compound chlorothalonil.

Samples were collected from the treated soil, the drop out drum, the scrubber and the carbon cartridges. The emissions from the plant were also sampled periodically.

Analysis.

Chlorophenols were extracted from the soil, converted to the acetates, and analysed on high resolution gas chromatography with electron capture detection (HRGC-ECD) and HRGC with low resolution mass spectrometry (LRMS) instruments. Organochlorine pesticides were extracted and analysed on HRGC-ECD and HRGC-LRMS instruments. Dioxins (PCDDs and PCDFs) were extracted using accelerated solvent extraction (ASE), cleaned up using a series of alumina, silica and carbon columns and analysed on HRGC with high resolution mass spectrometry (HRMS). Dioxin TEQ were calculated using I-TEF values.

Results and Discussion

Phase 1. Laboratory Study.

Detailed results of all the temperature, time and additive experiments will be presented elsewhere. The following results, Table 1, are from the experiments using an alkaline earth oxide additive that were scaled up in phase 2.

Table 1.

Sample	PCP (mg/kg)	Dioxin ($\mu\text{gTEQ/kg}$)
Feed soil	2900	74.9
T1 (400°C)	<0.01	1.57
T2 (450°C)	<0.01	0.083

These results show that the process of treating soil with a combination of the alkaline earth oxide additive at a temperature of 450°C for the set time period effected successful clean up. These parameters were used as the basis for the operating conditions in the pilot plant phase 2.

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Phase 2. Pilot Plant Study.

Results of the treated soils are summarised below. Detailed results of all the treated soil samples and the associated dust, scrubber and emission samples will be reported elsewhere.

Table 2 reports the results from the treatment of three soil types contaminated with PCP, dioxins and chlorothalonil. Feed soil (FS) and treated soil (TS) results from a range of feed rates (kg/hr) are presented.

Table 2.

Sample (Feed Rate)	PCP (mg/kg)	Dioxin ($\mu\text{gTEQ/kg}$)	Chlorothalonil (mg/kg)
Soil A FS	1440	17.1	
Soil A TS (40kg/hr)	<0.01	0.126	
Soil A TS (40kg/hr)	<0.01	0.027	
Soil A TS (60kg/hr)	<0.01	0.159	
Soil A TS (80kg/hr)	<0.01	0.232	
Soil A TS (80kg/hr)	<0.01	0.126	
Soil B FS	561	17.2	587
Soil B TS (40kg/hr)	<0.03	0.588	<0.1
Soil B TS (40kg/hr)	<0.01	0.061	<0.1
Soil B TS (60kg/hr)	<0.01	0.107	<0.1
Soil C FS	613	17.8	
Soil C TS (40kg/hr)	<0.01	0.121	
Soil C TS (60kg/hr)	<0.01	0.035	
Soil C TS (60kg/hr)	<0.01	0.081	

Table 3 reports the results of the soil/sawdust and sand/sawdust matrices and the matrix prepared from the sand and the consolidated drop-out dusts.

Table 3.

Sample (Feed Rate)	PCP (mg/kg)	Dioxin ($\mu\text{gTEQ/kg}$)
Soil C/10% sawdust FS	2020	190
Soil C/10% sawdust TS (60kg/hr)	<0.02	1.16
Sand/25% sawdust FS	3110	245
Sand/25% sawdust TS (60kg/hr)	<0.02	3.18
Sand/25% sawdust TS (60kg/hr)	<0.02	2.03
Sand/Drop-out dust FS	44.7	1280
Sand/Drop-out dust TS (60kg/hr)	<0.01	0.075
Sand/Drop-out dust TS (60kg/hr)	<0.01	0.057

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Table 4 reports the results of the matrix prepared with DDT and lindane. This matrix was prepared by the addition of known amounts of these pesticides to sand that was used as a clean material in the treatment plant.

Table 4.

Sample (Feed Rate)	DDT (mg/kg)	lindane (mg/kg)
Sand/Pesticide FS	482	241
Sand/Pesticide TS (60kg/hr)	0.0008	<0.00005

The results in Tables 1-4 clearly show that the treatment plant is effective in treating these matrices. The soils reported in Table 1 are typical of the range of soils likely to require treatment in New Zealand. In all cases the soils have been remediated to levels substantially less than the interim residential acceptance criteria of 0.05 mg/kg for PCP and 1.5µgTEQ/kg for dioxins.

While the treatment process is clearly effective it is of interest to study the changes in the dioxin profile that may be brought about by the action of the alkaline earth oxide additive on the chlorophenol and dioxin contaminants.

Figure 1 shows the contribution to PCDD toxic equivalents (TE) for the three feed soils. Figure 2 shows the contribution to PCDD TE for the treated soils. Note the change in the Y axis scale between Figure 1 and Figure 2. If these scales were the same in the two figures it would not be possible to observe the profile of the PCDDs in the treated soils.

Figure 1.

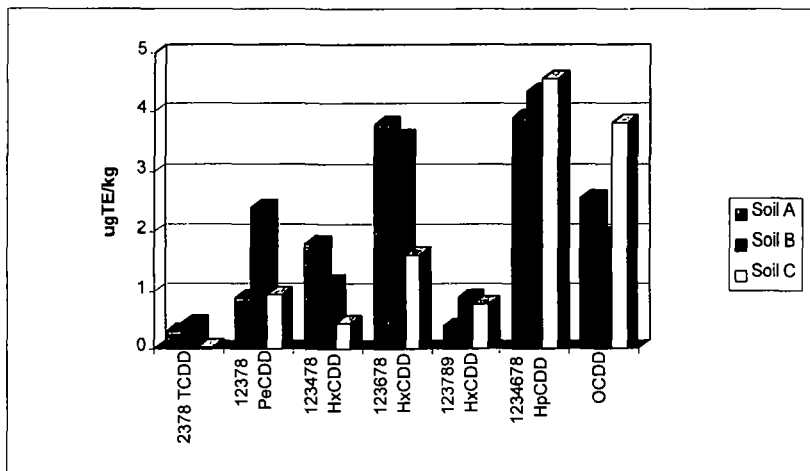
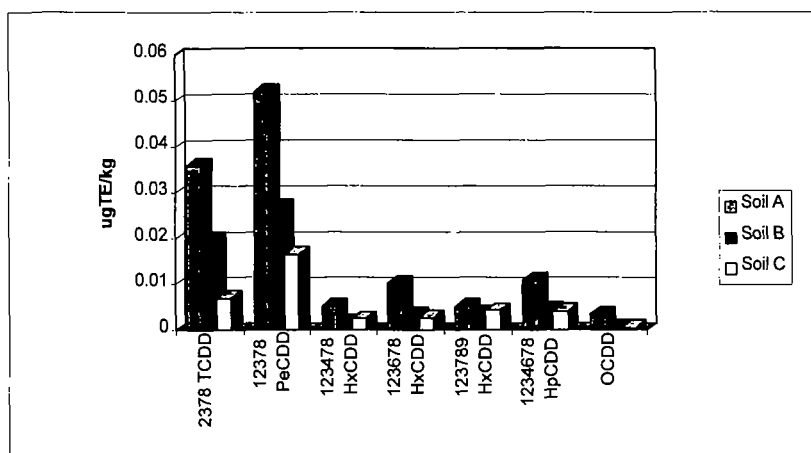


Figure 1 shows that all chlorination groups contribute to the TEQ with 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD the major contributors. These three compounds contribute about 90% of the TEQ in the feed soils.

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Figure 2 shows that in the treated soils all the chlorination groups contribute to the TEQ with 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD the major contributors. The hexa-, hepta and octa- chlorinated congeners now contribute less than 20% of the TEQ. The levels of the more toxic lower chlorinated congeners have also been reduced so that the overall reduction in dioxin TEQ in these soils ranges from 99.7 to 99.9% and is well below the acceptance criteria.

Figure 2.



Conclusion

There is effective treatment of all the organochlorine compounds that were contaminants in the matrices studied in this process.

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