

HEXACHLOROBENZENE DESTRUCTION WITH THE GEOMELT PROCESS

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ABSTRACT

Geosafe Australia Pty. Ltd. (Geosafe) and AMEC Engineering Pty. Ltd. (AMEC) have completed a series of three demonstration trials of a specially adapted version of the GeoMelt vitrification treatment process on concentrated hexachlorobenzene (HCB) wastes for Orica Australia Pty. Ltd. in Australia. The trials included HCB concentrations up to 33 wt% mixed in soil. The trials are in support of the Australian national strategy for the management of scheduled wastes as endorsed by the Australian and New Zealand Environment and Conservation Council.

The GeoMelt process used for this project involves the electric batch melting of a mixture of soil and HCB wastes in a refractory-lined crucible. The GeoMelt vitrification process has been used successfully on a wide range of contaminants such as polychlorinated biphenyls (PCBs), dioxins and pesticides. Operations involving the GeoMelt process in the USA and in Japan have demonstrated overall destruction and removal efficiencies in excess of 99.9999%.

Results from the HCB trials are promising and indicate that the GeoMelt process can effectively treat the HCB wastes. Destruction via dechlorination and pyrolysis reactions of HCB in the first step of the process (i.e. in the crucible) is the dominant treatment mechanism. Destruction efficiencies of >99.9% in this first step were achieved during the trials. Overall, a destruction and removal efficiency of >99.9999% was achieved during the trials for the complete treatment system (the melt and the off-gas treatment system).

INTRODUCTION

Geosafe Australia Pty. Ltd. (Geosafe) and AMEC Engineering Pty. Ltd. (AMEC) have completed a series of three demonstration trials of a specially adapted version of the GeoMelt vitrification treatment process on concentrated hexachlorobenzene (HCB) wastes for Orica Australia Pty. Ltd. in Australia. The trials were conducted in support of the Australian national strategy for the management of scheduled wastes as endorsed by the Australian and New Zealand Environment and Conservation Council [1]. This paper describes the approach taken and the results from the trials.

GEOMELT TECHNOLOGY DESCRIPTION

The GeoMelt process represents a group of vitrification technologies that can be configured in various ways to meet a wide range of treatment requirements. The original GeoMelt technology is In Situ Vitrification wherein contaminated soils and wastes are treated in place, in the ground. This base technology has been developed into other configurations that allow a wider range of treatment applications. All of the GeoMelt technologies involve the electric melting of contaminated soils and debris to result in the destruction, removal or permanent immobilisation of contaminants.

The melting process is initiated at the surface of a waste or soil mixture. Electrical power is directed to the treatment zone via graphite electrodes. Electrical power is regulated to maintain the desired melt rate. The melt temperature ranges from 1200-2000 degrees C depending on the materials being treated and the particular process configuration. The melt grows downward and outward until the electric power is shut off. Melt rates for full-scale treatment plants can exceed 100 tonnes per day depending on the configuration of the equipment and the material being treated. The melt sizes depend on the particular equipment configuration. Individual melts can reach up to 1000 tonnes in size.

Organic contaminants such as dioxins, pesticides and polychlorinated biphenyls (PCBs) are destroyed via pyrolysis and dechlorination reactions at elevated temperatures and in reducing conditions around the melt. No organic contaminants remain in the melt due to the inability of organics to exist at the temperatures involved. A broad range of organic contaminant types has been successfully treated in commercial operations. The destruction and removal efficiencies (DRE) achieved during commercial operations for all organic species are greater than 99.9999%. This DRE includes the percentage destroyed by the melt (typically 90-99.9%) and the percentage destroyed and/or removed from the off-gas stream by the off-gas treatment equipment.

Heavy metals and radionuclides are retained in the melt and are permanently immobilised in the resulting vitrified product. The vitrified product normally consists of a mixture of glass and crystalline materials. The product is typically ten times stronger than concrete and is extremely leach resistant.

Off-gases that evolve from the melt are collected in a steel containment hood and directed to an off-gas treatment system. The effectiveness of the melt in treating contaminants either through destruction for organic compounds or by immobilisation for heavy metals minimises the contaminant loading to the off-gas treatment system.

SUMMARY OF SELECTED ORGANO-CHLORINE APPLICATIONS

Polychlorinated Biphenyls (PCBs)

The GeoMelt-ISV process has been successfully used to treat PCB-contaminated soils and debris in the USA. One such project involved the treatment of 2,800 tonnes of contaminated soil and debris at a private Superfund site in EPA Region 10, Washington State. The maximum PCB concentration in the soil was 17,860 mg/kg. Liquid PCBs were poured into the soil to facilitate treatment. The project was evaluated by the United States Environmental Protection Agency

(USEPA) under the provisions of the National Toxic Substances Control Act (TSCA). The project was completed successfully and resulted in the USEPA granting Geosafe a National TSCA Operating Permit for the GeoMelt process to treat PCB-contaminated soils and wastes [2]. The GeoMelt process satisfied all performance criteria established for the project. The percentage of PCBs destroyed by the melt was 99.76% and the overall DRE was >99.9999%. Off-gas emissions met project requirements in that PCBs and congeners including dioxins and furans were below detectable limits. The vitrified product was determined to be free of PCBs. Finally, the process did not result in the contamination of the surrounding soil.

Dioxin, Hexachlorobenzene and Pentachlorophenol-Contaminated Soils

The GeoMelt process was successfully used in the USA to treat 5,400 tonnes of soil and debris at a Superfund Site in Salt Lake City, Utah. The site was a former industrial facility associated with the packaging and distribution of acids, caustics, organic solvents, pesticides, herbicides, fertilisers and other agricultural chemicals. The GeoMelt-ISV process was used to treat contaminated materials contained in an evaporation pond. The maximum measured concentration of any one contaminant was approximately 7,000 mg/kg for pentachlorophenol. Approximately 2,500 litres of an oily liquid contaminated with dioxins and furans was mixed with soil and staged in a central area of the pond for treatment. The operation was fully successful. Stack sampling results confirmed that there were no measurable concentrations of dioxins or furans (or other organo-chlorines) in the off-gas emissions. The entire volume of material was successfully treated and the surrounding soil was found to be free from contamination by the process [3].

Waste Agricultural Chemicals

As part of a waste treatment demonstration program, the GeoMelt process was tested in Japan on mixtures of waste agricultural chemicals. Contaminants included up to 33 wt% benzene hexachloride (Lindane), approximately 3.4 wt% of pesticides such as DDT, and heavy metals such as arsenic and lead. The tests confirmed a high destruction efficiency for the organo-chlorines. More than 99.9% of the benzene hexachloride and pesticides were destroyed by the melt prior to any off-gas treatment. The results indicate that the GeoMelt process would be expected to achieve an overall DRE for the organo-chlorines in excess of 99.9999%.

HEXACHLOROBENZENE WASTE

The HCB waste is a by-product of ICI Australia's chemical manufacturing operations conducted at Botany, near Sydney, from 1964 to 1991. The HCB wastes originated from the manufacture of carbon tetrachloride and perchlorethylene solvents. Approximately 8,200 tonnes of drummed HCB waste accumulated from those operations and is maintained in a secure warehouse in approximately 55,000 drums awaiting the development of a suitable treatment technology. Orica Australia Pty. Ltd. is now responsible for the HCB wastes. The principal problem with HCB is that it is a suspected carcinogen, is very resistant to degradation within the environment and can accumulate within the tissues of living organisms. The toxicity, relative stability, particular chemical properties and high concentration make it a particularly challenging waste to treat.

The drummed HCB waste primarily consists of hexachlorobenzene (>90%). However, the waste also includes weight percent concentrations of other organo-chlorines, such as

hexachlorobutadiene (HCB) and hexachloroethane (HCE). The HCB waste also includes polychlorinated biphenyls (PCB) at concentrations up to a few weight percent. The waste also includes high concentrations of dibenzo-p-dioxins and dibenzofurans that are on the order of 10-100 ng/g based on the international toxicity equivalent factors (i-TEF). The dominant species is octachlorodibenzofuran (OCDF) at concentrations up to approximately 30,000 ng/g on a mass basis or an i-TEF concentration of approximately 30 ng/g. A photograph of the HCB waste prior to its mixing with soil is shown in Figure 1.



Figure 1. HCB waste prior to mixing with soil

HCB DEMONSTRATION PROJECT

The project was undertaken in support of a national strategy for the management of scheduled wastes as endorsed by the Australian and New Zealand Environment and Conservation Council [1]. The objective of the project was to evaluate the treatment effectiveness of a specially adapted version of the GeoMelt process. Geosafe and AMEC undertook the project on behalf of Orica Australia Pty. Ltd. and SHE Pacific Pty. Ltd. SHE Pacific manages the project for Orica.

The project was conducted in accordance with a license issued by the South Australian Environment Protection Authority. The demonstration treatment facility was licensed in

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accordance with the Australian national protocol for licensing commercial facilities for the treatment of scheduled wastes. A detailed monitoring, sampling and analysis program was established to provide a comprehensive data package to evaluate the effectiveness of the treatment process.

The project involved a series of three trials with HCB concentrations in soil up to 33 wt%. The trials provided an opportunity to vary equipment and operational parameters to determine the most effective treatment configuration for the HCB waste.

HCB TREATMENT PROCESS

For this project Geosafe and AMEC employed a version of the GeoMelt Stationary Batch Process. This process involves electric batch melting of the soil and waste mixture in an above ground, refractory-lined crucible. For this demonstration project the process was approximately 1/10th scale.

The treatment approach used for the trials involved mixing the HCB waste with soil to prepare the waste stream feedstock. For one trial, the waste mixture included scrap steel, wood chips, plastic drum liners, used protective clothing and spent filters to simulate the expected waste mixture at full-scale. The soil/HCB mixture was then loaded into the crucible in preparation for treatment and an off-gas containment hood fitted above the crucible to collect off-gases. Graphite electrodes were then installed into the mixture and electrical power gradually applied. Full operating power was normally achieved in a few hours. Approximately 48 hours were required to treat a batch of waste. Thermocouples were positioned within the crucible to track the melt progress. During the operation off-gases were drawn from the crucible for treatment. The off-gas treatment system included the following steps: particulate filtration; thermal oxidation; quenching; multiple stages of high efficiency scrubbing; de-watering; and carbon adsorption. Electrical power to the melt was terminated when the melt had processed the entire volume within the crucible.

RESULTS

Three trials were conducted with HCB concentrations in soil ranging from 16.5 to 33 wt%. Each trial was designed differently to evaluate the effectiveness of different operating conditions to determine the most effective treatment approach.

Trial One

The first trial involved 16.5 wt% HCB mixed in soil. The results from the first trial showed that the GeoMelt process was effective in destroying the majority of the HCB as well as the other primary organo-chlorines in the waste. The destruction efficiencies calculated for the melt alone (without accounting for the off-gas treatment system) and the overall destruction and removal efficiencies inclusive of the melt and the off-gas treatment system are summarised in Table I.

Table I. Trial One Treatment Efficiencies for Primary Organo-Chlorines

Organo-chlorine	Melt Destruction Efficiency (DE)	Overall Destruction and Removal Efficiency (DRE)
Hexachlorobenzene (HCB)	97.52%	99.9997%
Hexachlorobutadiene (HCBD)	95.65%	>99.9999%
Hexachloroethane (HCE)	>99.9999%	>99.9999%

The percentage of HCB destroyed by the melt (97.52%) was reasonably satisfactory. The percentage of HCBD destroyed by the melt was quite good at 95.65% considering it has a significantly higher volatility compared to HCB. HCE, if present in the off-gases exiting the hood, was below detectable limits indicating a very high destruction efficiency.

The dechlorination and pyrolysis reactions that take place in the crucible were quite effective as evidenced by the fact that there were only trace amounts (<1%) of other species in the off-gas that would be derived from incomplete pyrolysis or incomplete dechlorination.

The overall DREs achieved for the primary organo-chlorines inclusive of the destruction by the melt and the destruction and removal by the off-gas treatment system were quite good. HCBD and HCE were not detected in the treated off-gases at the stack resulting in DREs in excess of 6-9s. The DRE value for HCB was nearly 6-9s. The license requirements were easily satisfied by approximately two or more orders of magnitude relative to the off-gas emissions of the primary organo-chlorines. A reasonable outcome was achieved with respect to dioxins and furans in the treated off-gases (0.55 ng/m³ i-TEF), but was expected to be improved in the second trial with modifications to the crucible cell design and to the off-gas treatment system.

The vitrified product was analysed to determine if it contained any residual organo-chlorines. The results established that there were no detectable traces of HCB or the other organo-chlorines in the product. Samples of the vitrified product were also subjected to the Toxicity Characteristic Leaching Procedure (TCLP) test. The TCLP results were significantly below the TCLP criteria, establishing that the vitrified product was acceptable.

Trial Two

The second trial involved HCB mixed in soil to achieve a maximum concentration of approximately 33 wt%. The HCB waste used in the trial varied significantly depending on the particular drum but, in general, the primary components were 80-90% HCB, 1-2% HCE, 2-4% HCBD, 4-5% Octochlorostyrene and approximately 2.5% PCBs.

The soil mixture in the crucible consisted of three zones, with each zone consisting of a different mixture and each zone being processed under different operating conditions. The purpose of using the three zones was to evaluate the treatment effectiveness under three different sets of conditions to help determine the most effective processing approach.

As with the first trial, the second trial demonstrated that the GeoMelt process was very effective in destroying the HCB as well as the other primary organo-chlorines in the waste. See Table II for a summary of the results.

Table II. Trial Two Treatment Efficiencies for HCB for the Three Treatment Zones

Treatment Zone	HCB Melt Destruction Efficiency (DE)	HCB Overall Destruction and Removal Efficiency (DRE)
One (16.5% HCB)	99.19%	>99.9999%
Two (16.5% HCB)	96.16%	Not measured
Three (33 wt% HCB)	98.82%	>99.9999%

When treating the HCB waste at a concentration in soil of 33 wt%, the overall destruction and removal efficiencies for the process exceeded 99.9999% for the primary organo-chlorines as none of the primary organo-chlorines were detected at the stack in the treated off-gases.

A good outcome was achieved with respect to dioxins and furans in the treated off-gas. When treating HCB at 33 wt%, the concentration of dioxins and furans in the treated off-gases was determined to be 0.04 ng/m³ i-TEF.

The vitrified product was analysed to determine if it contained any residual organo-chlorines. The results established that there were no detectable traces of HCB or the other organo-chlorines in the product. Samples of the vitrified product were also subjected to the Toxicity Characteristic Leaching Procedure (TCLP) test. The TCLP results were significantly below the TCLP criteria, establishing that the vitrified product was acceptable.

Trial Three

The third trial involved HCB mixed in soil to achieve a maximum concentration of approximately 33 wt%. In addition to soil and HCB waste, the waste mixture included scrap metal, wood chips, plastic drum liners, used protective clothing and spent filters. The addition of these materials is representative of what is expected at full-scale.

Unlike the second trial, the composition of the mixture was uniform throughout the treatment cell and did not include different zones. However, two different sets of operating conditions were used to assess the treatment effectiveness that resulted from each condition.

Untreated off-gases from the crucible were sampled twice during the trial and treated off-gases at the stack were sampled once during the trial. As with the first and second trials, the third trial demonstrated that the GeoMelt process was effective in destroying the HCB as well as the other primary organo-chlorines in the waste. A summary of the results is shown in Table III.

Table III. Trial Three Treatment Efficiencies for Primary Organo-Chlorines

Organo-chlorine	Melt Destruction Efficiency (DE)	Overall Destruction and Removal Efficiency (DRE)
Hexachlorobenzene (HCB)	99.52-99.73%	>99.9999%
Hexachlorobutadiene (HCBd)	98.09-99.65%	>99.9999%
Hexachloroethane (HCE)	99.78-99.99%	>99.9999%

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The destruction efficiencies for the melt alone prior to off-gas treatment were very good. The destruction efficiency from the melt alone of HCB exceeded 99.5%. The overall destruction and removal efficiencies for the process inclusive of the melt and the off-gas treatment system exceeded 99.9999% for the primary organo-chlorines. None of the primary organo-chlorines were detected at the stack in the treated off-gases. The result for dioxins and furans was 0.58 ng/m³ i-TEF. The performance with respect to dioxins and furans was reasonable given the difficult waste mixture and can be improved at full-scale with improvements to the design of the treatment plant.

The vitrified product was analysed to determine if it contained any residual organo-chlorines. The results established that there were no detectable traces of HCB or the other organo-chlorines in the product. Samples of the vitrified product were also subjected to the Toxicity Characteristic Leaching Procedure (TCLP) testing. The TCLP results were significantly below the TCLP criteria, establishing that the product was acceptable.

CONCLUSIONS

Results from the three trials indicate that the GeoMelt process can effectively treat the HCB waste.

The destruction of the HCB via dechlorination and or pyrolysis in the first step of the process (i.e. in the crucible) is clearly the dominant treatment mechanism. The majority of the waste is being destroyed in the first step and is not being volatilised to the off-gas treatment system.

The results also show that the reactions responsible for HCB destruction in the crucible are effective in that there are only trace amounts (<1%) of other species in the off-gas exiting the crucible that could be derived from incomplete pyrolysis or incomplete dechlorination.

Under the conditions of the trials, it was not apparent that significant amounts of volatile metal chlorides evolved from the crucible to the off-gas treatment system. The particular reaction scheme that was promoted in the crucible favoured the formation of HCl.

The vitrified product from all three trials was determined to not contain any measurable traces of HCB or the other organo-chlorines and the product easily satisfied TCLP leach testing criteria.

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WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

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