

Remediation of hydrocarbon contaminated soils and the development of an innovative thermal process.

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Abstract: An Australian company, Innova Soil Technology Pty Ltd, has developed an innovative Thermal Desorption Process to allow safe, reliable and efficient on-site treatment of hydrocarbon contaminated soils. The process is suitable for treatment of all organic based contaminants including petroleum hydrocarbons, polyaromatic hydrocarbons (PAHs), organo-chlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs). The innovative features of this process have resulted in increased energy efficiency, significantly reduced operating costs and superior emission control. With low operating costs, this process competes favourably with previously cheaper alternatives to treatment, such as off-site disposal and on-site containment. Significant technological advances on conventional directly heated thermal processes have yielded a system suitable for treatment of soils contaminated with non-chlorinated as well as chlorinated hydrocarbons. The process is designed to remediate the soil whilst ensuring that all stack gas and particulate emission standards will be met, particularly, $<0.1 \text{ ng/Nm}^3$ for Dioxins and Furans.

Keywords: Contaminated soils, hydrocarbons, thermal desorption, soil remediation, Dioxin.

1. INTRODUCTION

1.1. Background

Since the industrial revolution, and in particular, over the last 100 years, human technological endeavor has resulted in massive changes and sociological benefits. Hand in hand with these benefits have come particularly dangerous and deleterious impacts on our physical environment. As a result of accumulated industrial activity, our atmosphere has deteriorated, our waterways and oceans are polluted and significant portions of our land is contaminated with toxic chemicals. Air and water pollution problems are literally very visible, public awareness is high and consequently, extensive debate and significant positive actions, on a global scale, have resulted. In contrast, land contamination is very much a hidden problem. A problem no less significant, but because it is a "buried" one, far less public attention has been given to this negative environmental impact. Comments such as "while its underground, it's not bothering us" and "keep it contained" are typical of a public starved of factual information on the problems and ramifications of toxic substances in our soil.

Land contamination occurs when chemicals are present in the soil matrix that did occur naturally. Contaminated sites arise in a number of ways, many of which are the result of service industries, manufacturing and other industrial operations. Contaminated land has resulted from a multitude of operations associated with manufacturing, mining, gas and electricity, agricultural, military, commercial and domestic activities. As well as contaminated land issues, there is the related issue of treatment of contaminated material dredged from many of the world's industrial ports and harbours.

Common contaminants include organic sludges (containing petroleum products, oils, chlorinated solvents, etc.); oil, grease and tar (polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs)); pesticides and herbicides and many other chemicals and byproducts.

Invariably, contamination has resulted from inadvertent spillage and leakage (e.g. accidental spills, lagoon failures, contaminated runoff, etc.) during operations involving hazardous chemicals. But more alarmingly, much of the contamination has resulted from the dumping of waste materials.

In recent years, the problem of continuing land pollution is being addressed to some extent. Stringent environmental legislation, processing technology advances, environmental safety improvements and development of economically and ecologically sustainable practices to utilise wastes have all served to decrease the rate of generation of additional contaminated land. But the problem of what to do with the existing tracts of highly contaminated land remains with us as a major challenge.

1.2 *Contaminated land implications*

The presence of toxic chemicals in the ground affects our society in a number of ways, including,

Human health consequences:

- Carcinogenity (capable of causing cancer).
- Heritable genetic and chromosomal mutation (capable of causing mutations in genes and chromosomes that will be passed on to future generations).
- Developmental toxicity (capable of causing birth defects or miscarriages).
- Reproductive toxicity (capable of damaging the ability to reproduce).
- Acute toxicity (capable of causing death from even short term exposures).
- Chronic toxicity (capable of causing long-term damage other than cancer).
- Neurotoxicity (capable of causing harm to the nervous system).

Ecological implications:

- Environmental toxicity (capable of causing harm to wildlife and vegetation).
- Persistence (minimal break down and accumulation in portions of the environment).
- Bioaccumulation (accumulation, through repeated exposure in plants and animals).

Aesthetic impacts:

- Urban detriment (many contaminated sites present barren, ugly expanses in our cityscapes).
- Natural vegetation (inability for vegetation to grow on contaminated land).
- Accessibility (by virtue of the contamination many valuable sites are left unusable).

Toxic substances present in soil are affected by a complex set of processes including cross-media transfer, transformation and biological uptake. For instance, atmospheric pollution may result from emissions of contaminated dusts or volatile chemicals present in soils; surface water contamination may result from contaminated runoff or overland flow of chemicals; groundwater contamination may result from leaching of toxic chemicals in contaminated soil. Indeed, several different physical and chemical processes can affect contaminant migration from a contaminated site, consequently, contaminated soils can potentially impact on other environmental matrices.

1.3 *Extent of the problem*

Contaminated land issues exist throughout the world. Problems in the USA and parts of Europe have been particularly well documented with cases such as the “Love Canal” (USA) and Lekerke (Netherlands) receiving wide attention. Movies such as “A Civil Action” (Touchstone Pictures,

1998, John Travolta) and “Erin Brockovich” (Universal Pictures, 2000, Julia Roberts) have resulted in land contamination impacting our popular culture. Australia has extensive contaminated land problems as well. Most cities are littered with large tracts of land that lie idle because of the presence of toxic substances in the soil. Australia’s early reliance upon water transport has seen historical industrial land use based on, or near waterways. Consequently we find ourselves with many of our contaminated sites occupying valuable land in prime harbourside or waterfront locations.

We have known about some sites for many years, as evidenced by “the dumping of 400,000 gallons of toxic liquid waste, over a six week period, at the Homebush tip” reported in 1968 by the current affairs program 4 Corners, in a segment entitled “Fouling our own nest”. However, it has only been in the past decade that the true extent of the problem is being realised. Swane (1995) refers to more than 150 former gasworks sites in Australia requiring remediation. Smith’s (1993) review suggests that there are in excess of 7000 contaminated sites in the state of NSW with a total clean-up cost of \$2 billion. Victoria’s clean-up costs are estimated to be similar to NSW’s and that for the total country is thought to be between \$5 billion to \$8 billion.

2. CURRENT APPROACHES TO CONTAMINATED LAND PROBLEMS

The problem of continued soil contamination through industrial activity has been addressed to some extent through legislation and technological developments influencing the way industry operates. The problem of what to do with the current plethora of contaminated sites remains. There are two broad classes of methodologies currently employed to deal with the contaminated land issue; non-treatment methods and technology based solutions.

The non-treatment approaches involve containment or dumping. Containment involves lining or capping of a contaminated site, the toxic materials are basically left intact with this technique. Extensive future monitoring of a capped site is required, there is potential for leakage and the problem remains intact being preserved for future generations. The dumping option involves removal of the material to a hazardous waste dump and replacement with clean fill. This renders the site clean, by shifting the problem elsewhere. These approaches have been favoured over treatment methods as they currently present the cheapest available option.

Several treatment options for hydrocarbon contaminated land have been developed over the last 20 years. Methods include Thermal Desorption, Thermal Destruction (or Incineration), Soil Washing and Flushing, Chemical Treatment, Biological Remediation, Vacuum Extraction, Chemical Extraction and Solidification. Some techniques are well advanced and others are just emerging. Problems exist with effectiveness (bioremediation is not capable of successful treatment of some particularly dangerous substances such as polyaromatic hydrocarbons (PAHs)), suitability (some processes themselves use hazardous materials, such as hydrogen peroxide), public opinion (incineration is not widely accepted) as well as high costs.

All current treatment options are more expensive than the cost of containment or dumping. High remediation costs have meant that a third approach has been invariably adopted with contaminated land, i.e. leave it there.

3. THE DEVELOPMENT OF AN INNOVATIVE THERMAL PROCESS.

A Newcastle, Australia based company has developed a process to treat hydrocarbon contaminated land at costs significantly less than the current industry price. Innova Soil Technology Pty Ltd was founded in 1995 involving research and development with the University of Newcastle. Following

laboratory and pilot scale research, the company has developed an innovative, energy-efficient system to remediate land contaminated with carcinogenic and persistent hydrocarbon substances such as oils and tars. Innova's focus has been on process development intimately coupled with consideration of technological, economic, environmental and social issues.

The system is known as **D**irect-heated **F**ast-quenched **T**hermal **D**esorption (DFTD) and Innova has been awarded \$1.1million in Australian Government financial support from AusIndustry (the Department of Industry, Science and Resources) to demonstrate the capabilities of the treatment plant.

The treatment facility is fully mobile allowing on-site treatment of contaminated soil. This is very important from a social perspective as it alleviates the need for transportation of hazardous material to permanent facilities. Innova's developments have concentrated on energy efficiency, and operational stability. Resultant is a treatment process that now competes economically with the non-treatment options of dumping or capping. DFTD presents an "economic incentive" to *treat* rather than *dump* or *contain* toxic soils.

MCM Manufacturing Pty Ltd in Cardiff, NSW is currently fabricating the first treatment unit, which can treat 40 tonnes of soil per hour. The funding required to build the unit has been raised totally through local investment. The first unit will be completed in September 2001, when it will be used in a full-scale demonstration. Innova Soil Technology plans to be operating the unit on a commercial basis by 2002 and is currently discussing several large-scale Australian and international remediation projects.

3.1 Description of the DFTD process

The DFTD process, shown in Figure 1, involves heating the hydrocarbon impacted soil to separate the contaminants into the gas phase where they are subsequently converted into water and carbon dioxide. The conversion process is designed with a long residence time to allow complete conversion. Advanced off-gas treatment and dust collection systems have been developed to prevent contaminant reformation potential, resulting in a clean, dust-free, gaseous product stream. From a social and environmental perspective, it was essential to develop a process to treat the contaminated land problem while at the same time ensuring no negative impacts on air and water systems.

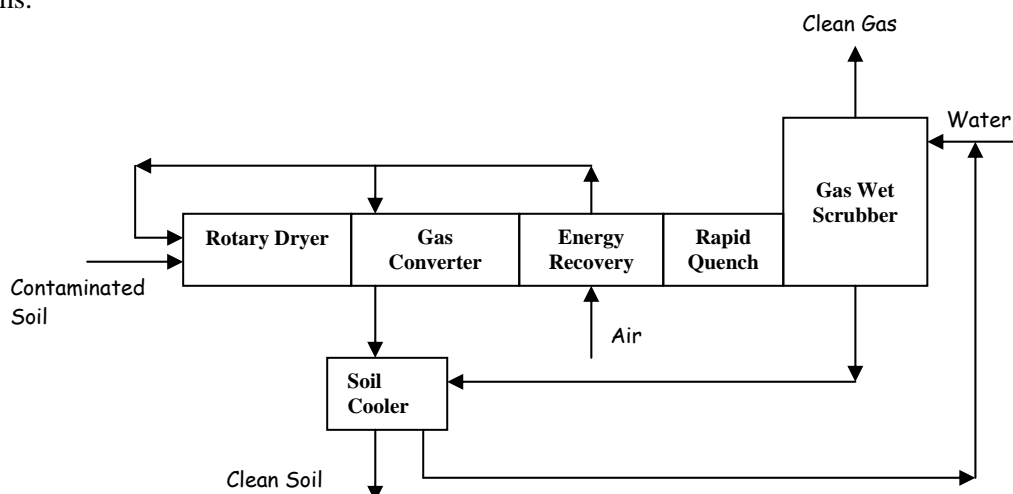


Figure 1. Schematic of the DFTD Process.

The DFTD process consists of series of integrated components designed to achieve successful contaminant separation to the gas phase, clean conversion of the gas stream, energy recovery, fines reconstitution with the parent soil and product cooling. Specifically, the system consists of:

- A direct heated rotary desorption unit – used to heat the soil thus separating contaminants from the soil matrix into the gas phase,
- A gas combustion chamber – with 3 seconds residence time at above 1050 °C, where the gas phase contaminants are converted to carbon dioxide and water,
- Energy recovery exchangers,
- A dry rapid gas quencher – off-gas cooling to eliminate gas phase contaminant reformation and dioxin formation potential,
- A scrubber with a wetted fan – to scrub the exhaust gases and collect particulates,
- A soil cooler –for both cooling and dust reconstitution with the parent soil.

The Innova system, consisting of proven and robust engineering components, is unique in its arrangement, allowing distinct operational advantages and superior emission control capability for the effective treatment of all types of hydrocarbon contaminated soils.

Significant measures have been taken to ensure efficient and reliable operation of the Innova DFTD system in terms of performance, safety and emissions monitoring and control. Features include continuous measurement of solids temperature, gas temperatures, pressure, gas flowrates, oxygen and CO/CO₂ levels plus outlet gas composition. Several levels of backup systems are employed for power and cooling water as well as an emergency “wet quench” system which ceases desorption, combustion and avoids gaseous atmospheric emissions in the case of plant failure.

4. GENERAL DIOXIN FORMATION ISSUES IN HIGH TEMPERATURE PROCESSES

Polychlorinated dibenzo-para-dioxins (PCDD) and furans (PCDF) are chlorinated, planar, aromatic compounds containing two benzene rings. The terms PCDD/F and “dioxins” carry the same meaning and are used interchangeably in the literature. There are many isomers of these compounds and it is recognised that those PCDD/F that have at least four chlorine atoms substituted in location 2,3,7,8 are the most toxic, an example of which is shown in figure 2.

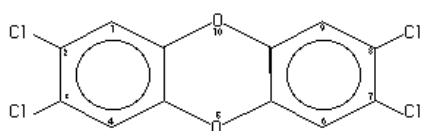


Figure 2: 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD)

With their high level of toxicity, dioxin formation in high temperature processes is a major issue. A plethora of literature exists in the area of dioxin emissions from high temperature processes. Specific uncertainties remain and the debate is active. Several reviews of the literature concerning toxicity, laboratory experimentation, mechanistic modelling, and emissions from industrial facilities have been conducted (eg Boening, 1998, Dyke et al, 1997, Dlugogorski & Kennedy, 1998). Several conclusions can be drawn from the literature, in broad terms:

- (i) Dioxin is a highly toxic substance and strict emission standards are required, a world’s best practice of process emissions not exceeding 0.1 ng/Nm³ should apply.

- (ii) Dioxin forms in combustion environments from hydrocarbon precursors with an availability of chlorine and oxygen.
- (iii) Dioxin is formed either through a homogeneous gas phase mechanism or through a heterogeneous (*de novo*) synthesis route, involving solid (particulate) surfaces.
- (iv) The gas phase formation reaction occurs at high temperatures (above 1000 °C), simultaneously with the gas phase destruction (combustion) reaction. At high temperatures the rate of destruction dominates the rate of formation.
- (v) A gas stream containing precursors (high-energy radicals, including chlorine), when cooled through the 600 °C to 200 °C temperature window in the presence of particulate surfaces, will yield dioxin through the *de novo* path, given sufficient time (1 second or more). Under these conditions, it is certain that dioxin will result; what remains uncertain is how much dioxin will result in a particular process and whether the reaction rates are sufficiently high to yield excessive dioxin emissions.
- (vi) Pre-1990 high temperature processes produced far more dioxin emissions than recently developed processes, which have had the advantage of new technological developments as well as a clearer scientific insight into dioxin formation mechanisms.

The conclusions from the current body of scientific knowledge are best summarised as: “Almost any combination of C, H, O and Cl can yield some polychlorinated dioxins/furans under *suitable* conditions of time and temperature” (Altwickler et al (1990)).

4.1 Dioxins and Conventional Direct Heated Thermal Desorption

Examining the above conclusions in the context of treatment of soils contaminated with chlorinated hydrocarbons using conventional direct heated thermal desorption processes, the following comments may be made:

Conventional direct heated thermal desorption involves direct heating of soils to achieve separation of the contaminants from the soil matrix to the gas phase. This is not a mass burning or incineration process, as the soil’s character and mechanical integrity remains intact (max. soil temperature around 550 °C) and the gas exists the system as a hydrocarbon rich flue gas at high temperature.

The gas stream passes through a fabric or ceramic filter baghouse¹ to remove particulates. A major constraint with conventional thermal desorption systems is that the kiln off-gas stream needs to be cooled below 400 °C² to protect the filter bags. This presents a major problem in terms of dioxin formation given the information on *de novo* dioxin synthesis in (v) above.

Next, there is a gas combustion step. The hydrocarbon laden gas stream is re-heated and combusted in a high temperature environment. This step is not a mass burning or incineration process, as only gases are involved. If the conditions of “1000+ °C for 1+ seconds” are not met, problems arise in

¹ In some configurations the baghouse is sometimes placed after the gas conversion phase, however, the same problems arise.

² Higher operating temperatures may be used in some configurations involving sintered stainless steel filters or ceramic filters, but these systems are expensive (stainless steel) or fragile (ceramic) and both are subject to damage by chemical reaction.

terms of complete conversion of the hydrocarbons to carbon dioxide and water. Incomplete combustion results in dioxin/VOC³ emissions.

After combustion, the exit gases are then passed to an outlet stack or scrubber to remove NO_x and SO_x and any remaining particulates. Two situations may arise where dioxin formation is an issue;

- (i) If the gases are slowly cooled in the stack/scrubber (ie between the 600 °C to 200 °C temperature window), dioxin will form.
- (ii) If the exhaust gases are kept above 750 °C in the exit stack, no dioxin formation will be detected in stack tests, but dioxin will form in the atmosphere above the stack as the gases cool slowly through the 600 °C to 200 °C temperature window.

In summary, the major problem associated with conventional direct-heated thermal desorption systems in treating soils contaminated with chlorinated hydrocarbons, is the uncertainty surrounding dioxin formation potential.

4.2 Dioxins and the DFTD System.

Innova's DFTD process is suitable for all organic based contaminants including petroleum hydrocarbons, PAHs, OCPs, dioxins and furans. Several measures have been employed to ensure that all EPA stack gas and particulate emission standards will be met, particularly, <0.1 ng/Nm³ for Dioxins and Furans. Specifically, the Innova process employs:

- A gas phase reaction chamber with 3 seconds residence time at above 1050 °C, ensuring complete conversion of the gas phase contaminants to carbon dioxide and water.
- A rapid (<30 ms) gas quench to cool the off-gas below 175 °C, eliminating the potential for contaminant reformation and dioxin formation in the reactive environment. The temperature effect of the rapid gas quench is illustrated in figure 3.
- The cooled (< 175 °C) gases are scrubbed via a large capacity, high efficiency, industrial spray scrubber, with wetted fan polishing, eliminating the need for a baghouse.



Figure 3. Schematic process gas temperature profile showing rapid gas quench.

³ VOC - Volatile Organic Compounds

5 COMPARISON OF DFTD AND CONVENTIONAL DESORPTION PROCESSES

There are several issues with conventional direct heated systems, particularly in terms of applicability in the treatment of chlorinated hydrocarbon contaminated soils. The DFTD system has addressed these issues, making it a safe and reliable option for the treatment of such material. Table 3 contains a comparison of conventional and Innova desorption systems in terms of several important issues of concern such as emission control (including dioxin suppression), operational reliability and efficient energy utilisation.

Table 1. Comparison of conventional and DFTD systems with respect to several issues of concern.

Conventional Thermal Desorption Systems	Innova DTFD System
<i>1. Gas cooling and emissions - baghouse, scrubber or stack.</i>	
Gases entering a baghouse, stack or scrubber are slow cooled; this raises immediate concerns about dioxin formation. This issue is significant where aromatic or chlorinated hydrocarbons are present in the soil. In these cases, dioxin will form when gases are cooled through the 600 °C to 200 °C temperature window in around 1 second. There is scientific debate as to how much dioxin forms and if indeed it is below the gas emission standard of 0.1 ng per m ³ . There remains uncertainty.	DFTD employs a very rapid dry gas cooling system, the gases are cooled to below 175 °C in less than 30 milliseconds, eliminating any potential for dioxin formation in the reactive environment. The final exhaust gases enter the wet scrubbing system at < 175 °C, too low a temperature for any dioxin formation to occur. There is no uncertainty about rapid gas cooling – if this is done, no dioxin will form and the emission standards of 0.1 ng per m ³ will be met.
<i>2. Baghouse - reliability</i>	
Baghouses are prone to clogging and filter media damage, yielding operational difficulties.	DFTD uses an industrial wet scrubber to remove particulates. The wet stream produced is used to both cool the soil and reconstitute the collected particulates with the bulk soil. Steam produced is condensed and recycled to the scrubber.
<i>3. Rotary kiln – performance</i>	
Some conventional designs have soil temperature limitations and may be prone to operational problems such as overheating when processing soils with high hydrocarbon content.	The rotary dryer used in the DFTD system is designed to provide efficient heat transfer into, and, mass transfer out of the soil, yielding enhanced desorption. The system is operated to ensure no overheating.
<i>4. Baghouse – thermal efficiency</i>	
The presence of the baghouse necessitates a cycle of <i>heating → cooling → heating → cooling</i> , which is not energy efficient.	With the wet scrubber replacing the baghouse, there is no cycling in the DFTD process, only <i>heating → cooling</i> . This improves energy efficiency and thus operating costs, reliability and Greenhouse gas emissions.
<i>5. Energy recovery</i>	
Conventional systems do not have energy recovery from the product gas.	By heat exchange, Innova recycles energy to the burners, thus reducing the amount of fuel required and thus the operating cost and Greenhouse gas emissions.
<i>6. Feed material characterisation</i>	
Conventional systems are generally operated as a “stand-alone” process plant relying on standard environmental assessments of the contaminated site for information on the incoming feed material.	Innova has established a unique suite of characterisation techniques, designed to yield an understanding of the behavior of the particular soil in the DFTD process. This assists in setting suitable operating parameters to enable the plant to operate safely and efficiently.

6. CONCLUSIONS

Contaminated land issues exist throughout the world, having arisen from prior industrial activities. The presence of toxic chemicals in the ground has significant human health, ecological and aesthetic implications. The current approaches to dealing with the problems involve, non-treatment options (shift or contain the problem), various treatment processes (inhibited by factors such as high costs) or inaction.

Innova Soil Technology Pty Ltd. has developed a new thermal desorption system that addresses issues of energy efficiency, operational reliability and dioxin formation, resulting in a *cost-effective* process suitable for the efficient and safe treatment of hydrocarbon contaminated soils, *including* those contaminated with chlorinated substances.

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