

Treatment of Organic Hazardous Wastes in Vietnam - Test Burn in a Cement Kiln

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Abstract

Mismanagement of hazardous wastes constitutes a serious threat to health, environment and economic growth in many developing countries. In the Southern Focus Economic Zone, comprising the most rapidly growing provinces of Vietnam,

Ho Chi Minh City, Dong Nai, Binh Duong and Vung Tau, approximately 30,000 industrial enterprises produces more than 70,000 tonnes of hazardous wastes yearly without having any large scale environmentally sound treatment options available. The feasibility of using a modern local cement kiln for environmentally sound destruction of organic hazardous wastes was investigated in this study.

Both the EU and the US regulation on hazardous waste management consider cement kilns to be a sound option for hazardous waste disposal. However, the regulatory approach differs between the two continents. The emission limit values for dioxins and furans are slightly more stringent in the EU regulation than in the US, however no test burn is required for performance verification in EU. The US permitting process, including test burn, is time consuming, complex and expensive. A modified approach, combining the best from the EU and the US regulation, together with national requirements was applied when testing the feasibility of a modern cement kiln in South of Vietnam in 2003.

A baseline study and a one-run test burn was carried out to investigate the destruction performance of the kiln under normal operating conditions. A solvent-based insecticide containing two aromatic molecules, one with chlorine and fluorine was used as a candidate for the test burn. None of the insecticides was detected in the exit gas and the destruction and removal efficiency DRE was measured to be better than 99.999985%. In comparison, the US regulation requires a DRE of 99.99% for these two insecticides.

The Stockholm Convention on persistent organic pollutants (POP's) requires "*complete destruction and irreversible transformation*" of POP's and POP's waste as well as minimisation and avoidance of emissions of dioxins, furans, PCB's and Hexachlorobenzene during disposal. The test burn demonstrated that all these

compounds were below the detection limit and that the destruction had been complete and irreversible, i.e. no new formation of dioxins, furans or PCB's. With the exception of NO_x, which was slightly higher than the emission limit value all other measured parameters were low compared with international standards and in full compliance with the Vietnamese emission limit values.

The test burn demonstrated the suitability of the Holcim cement kiln to co-process hazardous wastes and that a controlled substitution of fossil fuel with organic hazardous waste didn't affect the emissions. The co-processing option is immediately available to treat a considerable amount of the hazardous wastes currently generated in South Vietnam.

Keywords: Hazardous Waste Management; Developing countries; Regulatory requirements; Test Burn; Organic Hazardous Compounds; Cement Kiln.

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1. Introduction

The development of a proper hazardous waste management infrastructure in developing countries is not only required to protect human health and the environment but it is also necessary to sustain further development of their economies. The degree to which developing countries have proper rules and regulations in place varies widely from country to country. In many of the developing countries, even when rules and regulations are in place, enforcement of such regulations is weak.

This is the also the situation in Vietnam; the regulatory requirements of Decision 155 (1999) on Hazardous Waste Management have not yet been implemented. The monitoring and enforcement practices are weak, and together with lack of awareness, this means that companies are not properly managing their hazardous waste because of their lack of knowledge on what types of waste are hazardous and how to properly segregate, store and manage the waste.

A national survey conducted in 1999 revealed that most factories and enterprises of the main industrial sectors and the craft villages do not have sufficient treatment facilities and therefore release into environment considerable amount of hazardous waste. This is compounded by infectious waste from hospitals and the unsafe storage and disposal of agricultural chemicals and their containers in the mobile incinerator of Ministry of Defence (Karstensen et al., 2003b; Khanh, 2000; Kunisue et al., 2003; Quyen et al., 1995; Thiruchelvam et al., 2003; World Bank, 2004;).

Due to serious concern about the deterioration of the environment, the Peoples Committee of Ho Chi Minh City initiated an environmental improvement project where one objective was to develop a Master Plan for Hazardous Waste Management. The Southern Focus Economic Zone (SFEZ) of Vietnam comprises Ho Chi Minh City (HCMC), Dong Nai, Binh Duong and Ba Ria Vung Tau, which are the major industrial provinces in Vietnam with the highest growth rate. The population of the SFEZ is approximately 8.6 million, which together with the industry is putting pressure on the existing waste management facilities for all types of waste (World Bank, 2004; Yen et al., 1996).

The region is characterised by very high number of small and medium size enterprises SME's whereof almost 30,000 are located in HCMC alone (HCMC,

2002). When the preparation of the Hazardous Waste Master Plan started in 2002, there was no information available on the quantities of hazardous waste generated in industry enterprises in the area. In addition to industry there are 137 hospitals and 10,592 small clinics in the region. The findings also showed that the industry produces more than 70,000 tonnes of hazardous wastes yearly and that current practices and facilities were inadequate and that the hazardous waste issue will become much more serious if no actions are taken (Karstensen et al., 2003a). The surveys confirmed that all the essential components of a hazardous waste management system need to be improved. A few hazardous waste management companies are in operation, including some smaller incinerator facilities, but they are not technical updated and their environmental performance is not satisfactory (Karstensen et al., 2003a).

Due to the urgent needs identified a joint project between Central Ministries, Provincial Departments and Holcim Cement was initiated to investigate the feasibility of using a modern local cement kiln for treatment of organic hazardous wastes. A test burn following a modified regulatory scheme was carried out in October 2003. The objective of the test was communicated transparently to all stakeholders and the burn was inspected by scientists from universities and research institutes in Vietnam.

2. Hazardous waste management in Ho Chi Minh City

The economy of Vietnam has gradually been changed from a centrally planned system to a socialist oriented market economy. In the period 1991-2000, Vietnam's gross domestic product (GDP) increased with 7.5% annually. In 2004 the growth in GDP was 7.7% in total, with 3.5% growth in the agriculture sector and 10.2% in the

industry sector (Saigon Times weekly, 2005). In Ho Chi Minh City and the surrounding provinces, the growth in industry has been above 15% the last years.

The Hazardous Waste Master Plan proposed technical, financial and institutional arrangements for implementing a regional hazardous waste system for the SFEZ, including collection, storage, pre-treatment, reuse/recycling options and final disposal facilities. The plan also proposed a financing and cost recovery system (Karstensen et al., 2003a). The preparation started with an inventory and a review of the current practice, done through a series of site visits and interviews of experts and personnel involved in waste management. Surveys were carried out in 12 waste management companies, 7 industrial zone authorities and 88 industrial waste generators. Waste generators in the following sectors were surveyed:

Table 1	N	Industry
	8	Oil and gas industry
	3	Steel manufacturing
	3	Shipbuilding and mechanics
	4	Oil-fired power plants
	7	Pesticide produces
	7	Iron / metal industry
	6	Mechanical industries
	1	Construction materials
	6	Electronics industry
	6	Footwear producers
	10	Chemical industry
	10	Electroplating / galvanising

5	Paper producers
7	Textile industries
4	Leather production facilities
1	Electrical transformer

The aim was to obtain information of the types of process used in the different sectors; the waste generated, and waste management practices at the waste generators. Based on the survey information "waste factors" was derived for the different sectors, representing a typical quantity of waste generated per employee or per unit of production. This was scaled up to estimate roughly the total waste generated by multiplying the waste factor by the total number of employees or total units of production. The surveys showed that approximately 73,000 tons of hazardous wastes were generated in SFEZ in 2002; a number estimated to increase to approximately 310,000 tons in 2012 taking into account projected industry growth. Approximately 50% of the waste was oil-based.

Socio-economic considerations were factored into the evaluation of the hazardous waste management options. Economic impacts on all affected parties, including the public at large, were assessed. Indirect costs and non-economic benefits were also considered. Environmentally Sound Management principles (ESM) is defined as a concept for ensuring that wastes are managed in a manner which will save natural resources and protect human health and the environment against adverse effects which may result from the management of such wastes and materials. Based on ESM principles, the Master Plan recommended developing hazardous waste treatment options through private investments. One potential treatment options

recommended to investigate further was the new Holcim cement plant in Kien Giang Province (Karstensen et al., 2003a).

3. Obsolete pesticides in Vietnam

The green revolution in rice farming was initiated in Vietnam in the 1960's and plays a significant role in intensive cultivation of rice and other short-seasoned crops. However, intensive farming is inevitably associated with extensive pesticide use and despite the many achievements in pesticide management farmers still regard pesticides as indispensable (Community Integrated Pesticide Management, 2001). Vietnam, like other developing countries, faces many pesticide problems. Pesticides have been used since the 1940's and in 1957 the use were reported to be 100 tons per year. By 2000 this had grown to more than 30,000 tons and with further economic growth it is reasonable to anticipate that the consumption of pesticides will increase further (Adger, 1999; Berg, 2001; Berg, 2002; GINC, 2001; Morton and Blackmore, 2001; Mele and Lenteren, 2002).

Before 1990, no pesticide management regulations were in place in Vietnam. With government subsidies, pesticides were imported and distributed to farmers by state agencies. The pesticide use in 1990 was 15,000 tons of finished products, including those in the WHO categories classified to be extremely hazardous. These included Methyl Parathion, Monocrotophos and Methamidophos, as well as the highly persistent DDT and HCH (GINC, 2001; Nguyen and Dao, 2002).

Reviews highlight some major problems of pesticide management in the country such as: lack of facilities to deal with obsolete and confiscated pesticides; difficulties in export and domestic consumption of vegetables and fruits due to

pesticide residues; smuggling of pesticides across the borders; inadequate pesticide stores to meet the environmental safety conditions; small labels with unintelligible print and safety symbols, spraying of pesticides without any protective clothing such as gloves and face masks and in doses up to 20 times more than recommended. According to the Ministry of Health, some 345 people were killed and more than 8,000 people became seriously ill in 1999 as a direct result of using pesticides (Bolay et al., 1997; Cue et al., 1998; DoSTE, 1998; Finizio, 2002).

From 1961 to 1971, the US and South Vietnamese armies sprayed millions of liters of toxic herbicides, mainly Agent Orange, over approximately 10% of South Vietnam to destroy the dense tropical forests and crops that provided cover and food for combatants. According to official US reports, "Operation Ranch Hand," as the spraying programs were called, destroyed 14% of South Vietnam's forests, including 50% of the mangrove forests. Researchers at Colombia University have dramatically increased estimates of both the levels of exposure and the number of people sprayed with Agent Orange during the Vietnam War. Stellman et al. (2003) reports the dioxin contaminants to be as much as four times higher than previous estimates, and mapped villages in which 2.1 million to 4.8 million people were directly sprayed with the herbicides. About 65% of the herbicides were 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), which contains TCDD, the most dangerous form of dioxin. In the US, Vietnam veterans are now compensated for ten diseases that have been linked to exposures from spraying in Vietnam (Kang et al., 2001). A 2001 study by U.S. and Vietnamese government scientists found alarming levels of dioxin in the blood of residents of Dong Nai province, even among those who didn't live there during the Vietnam War or were born after the war ended (Dwernychuk et al., 2002).

An initial inventory of accumulated obsolete pesticides and contaminated soil was done in Vietnam in 2001-2003 by the Vietnam Environment Protection Agency (VEPA) and the Plant Protection Department (Karstensen et al., 2003b). The inventory showed that approximately 10,000 tons of highly dioxin-contaminated soil stemming from herbicide spillage during the War is still not treated, and more than 225 tons of 200 different obsolete pesticides and 1.7 million containers are currently accumulated in 100 locations in Vietnam (Karstensen et al., 2003b). Most of the stockpiled obsolete pesticides are mixed and the POP's content (UNEP, 2001) is estimated to constitute approximately 8 tons.

DDT import was banned in 1992 but most of the stockpiles were allowed to clear the system resulting in use termination probably before 1995. Deltamethrin, Vectron, Icon, and Pyrethroid are now used as substitutes for DDT, but still some obsolete stocks of DDT remains. This may explain, at least partly, why elevated concentrations of DDT and other organochlorines are frequently found in biological and environmental samples in Vietnam (Minh et al., 2004; Hung and Thiemann, 2002; Nhan et al., 1998; Nhan et al., 1999). Vietnam has signed and ratified the Stockholm Convention on POPs (UNEP, 2001) and does not manufacture or "legally" use any of the POPs pesticides but some find their way, probably due to smuggling.

The Ministry of Defence is currently providing a disposal service to the Provinces of Vietnam. The disposal involves all kinds of hazardous chemicals and obsolete pesticides and must be requested by the Peoples Committee of the Provinces. The disposal is done in a mobile incinerator with two chambers. The incinerator is fired with oil and claimed to reach a temperature of 800°C in the secondary chamber. The flue gas treatment is confined to simple water scrubbing system and a low stack

for emission dispersion. Residues are landfilled. The incinerator has low capacity (kilograms per hour) and must be fed manually and is run discontinuously.

4. Test burn with hazardous wastes in a Vietnamese cement kiln

A joint project with representatives of the authorities and Holcim Cement Company was initiated and the objective was to carry out a test burn to investigate if the cement kiln was able to co-process hazardous wastes in an irreversible and environmental sound manner, i.e. with no influence on the emissions when fossil fuel was partly replaced by hazardous waste.

The project group consisted of experts and managers in relevant Governmental Ministries and Provincial Departments and was supervising the planning and the execution of the 10 month project. Information about the test burn was disseminated well in advance to all relevant stakeholders and the actual test burn was inspected by scientists from the most prominent universities and research institutes in Vietnam.

A prerequisite for getting approval to carry out the test burn was that sampling and analysis should be done by an independent and qualified third party and that the following preconditions at the cement plant in Hon Chon was fulfilled:

- 1) The technical process and the chemistry were considered to be feasible for co-processing of hazardous wastes.
- 2) Power and water supply were stable and adequate.

- 3) The waste receiving, handling, storage and introduction process were considered to be stable, safe and robust.
- 4) All involved staff and subcontractors had received adequate information and training and the project objective was communicated transparently to all stakeholders.
- 5) Emergency procedures were implemented and followed, i.e. personal protective gear was used and fire extinguishing and equipment/ material for cleaning up spills were available.
- 6) Procedures for stopping waste feed in the event of an equipment malfunction or other emergency were implemented. The set points for each operating parameter that would activate feed cut-off were specified.

4.1 Plant description

The Holcim cement plant is located about 300 km west of Ho Chi Minh City, in Hon Chong, Kien Giang Province and produces cement clinker in a dry suspension preheater rotary cement kiln equipped with a precalciner. The kiln rotates with a speed of 3.5 rounds per minute, is 4.6 meter in diameter, 72 meter long with a 110 meter high double string 5-stage preheater tower and produces approximately 4,400 tonnes of clinker per day.

The kiln and the precalciner are fired with coal through the main primary burner and the secondary precalciner burner. The main burner is a Pillard Rotaflam

three channel burner, usually fired with 7 tons coal per hour; the precalciner 13 tons per hour. The normal fuel consists of anthracite coal with an average calorific value of 30 MJ/kg.

The gas flows in the system provides combustion air to the main burner and the precalciner, and is primarily taken from cooling air in the clinker cooler which ensures maximum heat recovery. Under normal operation, the exit gas from the preheater is directed through a conditioning tower to the raw material mill and the coal mill for drying purpose. A small portion of the gas (8%) can be directed to a bypass system to reduce build-up of chlorine and alkalis. After drying, the gas is dedusted in high efficiency electro static precipitator (ESP) before entering the main stack.

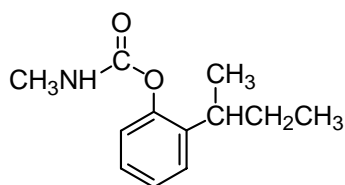
The production process is monitored and controlled through an advanced control system with continuous on-line monitoring of the following parameters: the kiln inlet gas is analysed for temperature, O₂, CO and NO_x; the preheater outlet gas for temperature, O₂, CO and NO_x and the stack outlet gas for temperature, O₂, CO, CO₂, NO, NO₂, SO₂, HCL, NH₃, H₂O and volatile organic carbon (VOC). The main stack is 122 meter high and approximately 4 meter in diameter.

4.2 Test burn candidate

The purpose of the test burn was to investigate if the kiln was able to co-process hazardous wastes in an irreversible and environmental sound manner, i.e. to compare the emissions under normal baseline conditions when only fossil fuel was used with the emissions when fossil fuel was partly replaced by a hazardous waste.

The greatest challenge in the first phase of the project was to identify a suitable local available test burn candidate which could fit the purpose. Finally a solvent-based insecticide with two active ingredients, 18.8% Fenobucarb and 2.4% Fipronil, was identified at an international pesticide company in Dong Nai Province, North of Ho Chi Minh City. The active ingredients of the insecticide consisted of two different aromatic molecules solved in Cyclohexanone and aromatic solvents. The concentration was regarded to be sufficient to be able to demonstrate the necessary DRE of 99.99%. The insecticide had expired, was deemed unusable and approximately 40,000 litres was stored in 200 steel drums at the pesticide company waiting for a treatment option.

Fenobucarb has a molecular weight of 207.3 with the sum molecular formula $C_{12}H_{17}NO_2$.



ig. 1 Chemical structure of Fenobucarb.

Fipronil has a molecular weight of 437.2 with the sum molecular formula $C_{12}H_4Cl_2F_6N_4OS$ and containing 16.2% chlorine and 26.06% fluorine.

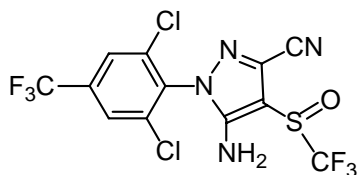


Fig. 2 Chemical structure of Fipronil.

Fenobucarb and Fipronil contain 6.7% and 12.8% nitrogen respectively. Quantitative and qualitative analysis of the active ingredient is usually done by HPLC with UV detection or by GC with electron capture detection ECD (Vilchez et al., 2001; Kawata et al., 1995).

The insecticide product had been screened through 0.25 mm sieve and was in true solution. No settlements, particles or polymerization or degradation of the active ingredient was observed. The analysis result established by the Plant Protection Department in Ho Chi Minh City confirmed that the product was homogenous and contained 18.8% Fenobucarb and 2.4% Fipronil.

Both Fenobucarb and Fipronil are sold as active ingredients in separate insecticide formulations and they are potent insect killers, with different mechanisms and reaction time. Both active insecticide ingredients are classified by the World Health Organisation to be moderately hazardous (class II) on their scale from extremely to slightly hazardous (WHO, 2002). The insecticide was considered to be a representative candidate of the hazardous waste streams which needs a treatment option in Vietnam to day (Karstensen et al., 2003b) as well as being a good candidate for verification of the cement kiln destruction capability consisting of stable aromatic molecules, one containing chlorine and fluorine. The other requirement of the test burn candidate which was decided beforehand was the need of sufficient amounts and concentration of a homogeneous hazardous compound. The insecticide was a free flowing liquid with a viscosity similar to water and easy to pump through a separate channel in the main burner. The calorific value of the insecticide was measured to be 36.6–38.1 mega Joule per kilogram (after the test burn), mainly due to the solvents. Fine coal used in the cement plant was by comparison 30 mega Joule per kilogram.

Prior to the test burn a 16m³ steel tank for storage and feeding of the hazardous insecticide was build. The tank was connected to the light fuel oil pumping system with automatic dosage and switch off/on through the main control system. The tank was equipped with a diaphragm pumping system to empty the drums and was placed in a bunded concrete construction for spill recovery. The insecticide was pumped from the tank through stainless steel pipes to the burner platform, through a calibrated flow meter and into the main primary flame together with coal through a three channel burner. The transport of the 200 drums of insecticide from Dong Nai to Kien Giang was carried out by 10 trucks and organised by the owner of the insecticide. The emptying of the insecticide from the drums to the tank was carried out by trained personnel. Safety during transportation, handling and transfer had the highest priority and due care was demonstrated during the course of the test. Personnel were equipped with personnel protective gear including organic vapour cartridge face masks. Preventive measures were in place in case of exposure, spillage and fire. All installations and drums were earthed during the transfer of the pesticide to the tank. All empty drums were taken back to the owner in Dong Nai by the same trucks.

4.3 Outline of the test burn

The entire test was conducted over two days, 16 and 17 October 2003, starting with a baseline study with coal as fuel only and then the test burn the second day were parts of the coal was substituted by the insecticide. The plant was run both days in a normal mode, i.e. whit the kiln gases directed through the raw mill for drying.

A few days before the start of the test campaign the pumps and flow meters were calibrated using light fuel oil and all monitors were checked. An Australian independent and accredited test company were hired to carry out the stack gas sampling. They subcontracted other accredited laboratories in Australia and Europe to do the analysis. The entire testing and analysis complied with the US and EU standards.

The trucks with the insecticide arrived the day before the test burn and the emptying of the drums were done manually with a steel lance, chemical resistant hose and a diaphragm pump connected directly to the storage tank. The sampling team arrived the day before the baseline test and began to set up the sampling and monitoring equipment. The second day of the test, insecticide was introduced to the kiln starting with 1,000 litres per hour and increasing to 2,000 litres per hour some hours before the stack sampling started. During the stack sampling campaign, between 11:09 AM and 18:13 PM, 2,030 liters of insecticide was introduced through the main burner per hour. After the sampling was finished the feeding rate was increased to approximately 2,500 litres per hour and in total 39,500 litres was fed to the kiln in less than 20 hours. After emptying, tank and pipes were cleaned with light fuel and fed to the kiln.

4.3.1 Process and sampling conditions during testing

Each hour, 292 tons of raw meal was fed to the preheater and 179 tons of clinker was produced during the entire test. Feeding of coal to the secondary precalciner burner was stable at 13 tons per hour both days; the coal feed to the main

primary burner was reduced by 1.5 tons from 7 to 5.5 tons when the insecticide was introduced to compensate for the heat input.

Due to an analysis error of the heat content of the solvent of the insecticide the coal to the main burner was not reduced sufficiently during the test burn. Measurements prior to the test burn had shown a calorific value of approximately 22.5 mega Joule for the insecticide but during the test it was realised that this had to be wrong because the temperature of the kiln increased. This was confirmed by new analysis after the test burn when the calorific value of the insecticide was measured at several laboratories to be 36.6–38.1 mega Joule per kilogram; fine coal is by comparison 30 mega Joule per kilogram, i.e. the coal feed to the main burner should have been reduced by approximately 2.5 tons to balance the heat requirement.

The Australian test company followed stringent quality assurance and control (QA/QC) procedures throughout the monitoring program. These procedures covered sampling procedures and equipment, maintenance of sample conditions and concealment, storage and freight of collected samples etc. The sampling of solid process samples, i.e. raw meal, clinker, fine coal, and dust from the ESP's was carried out by the plant staff. The testing conditions and stack values recorded during the two test days are given in table 1.

Table 1 Testing conditions and stack values

	Baseline	Test burn
	16 October	17 October
<i>Sampling time</i>	10:00–17.15	11:09-18:13
<i>Velocity at sampling plane (m/s)</i>	11.2	11.9
<i>Moisture content (% v/v)</i>	12.2	12.3

<i>Gas flow rate at STP* & 10% O2 (Nm³/hour)</i>	456,000	485,000
<u><i>Average oxygen concentration (%v/v)</i></u>	<u>5.24</u>	<u>5.21</u>

* STP – standard temperature and pressure.

Gas velocity and volume flow rate were determined in accordance with US EPA Method 2, positions for velocity pressure and temperature measurement are determined in accordance with US EPA Method 1 and stack gas moisture content was determined in accordance with US EPA Method 4 (Federal Register, 2000).

4.4 Emissions results and discussion

The results of stack gas sampling for the two days are compared with the current emission limit values (ELV) in the Vietnamese standard TCVN 5939-1995 and 5940-1995.

4.4.1 Destruction and removal efficiency of the insecticides

To make sure that Fenobucarb and Fipronil was not a product of incomplete combustion normally found in the stack emissions, Fenobucarb and Fipronil were also analysed in the samples taken on the 16 October, i.e. when they were not introduced.

The destruction and removal efficiency (DRE) of Fenobucarb and Fipronil in the process is calculated according to the following equation:

$$\text{DRE} = [(W_{\text{in}} - W_{\text{out}}) / W_{\text{in}}] \times 100$$

were W_{in} is the mass of Fenobucarb and Fipronil entering the kiln and W_{out} is the mass exiting the stack gas.

The introduction of 2,030 litre insecticide per hour amounts to 362 kg pure Fenobucarb and 46.2 kg pure Fipronil per hour when corrected for the density, 0.95 (kg/l). No Fenobucarb or Fipronil were detected in the exit gas and the detection limit was 21 ng/m³ for Fenobucarb and 14 ng/m³ for Fipronil and this amounts to less than 0.0101808 gram of Fenobucarb and less than 0.0067872 gram of Fipronil per hour, which constitute a destruction and removal efficiency of better than 99.999997% and 99.999985% for Fenobucarb and Fipronil respectively.

Table 2 Analysis results Fenobucarb and Fipronil in the stack

	Baseline (ng/m ³)	Test Burn (ng/m ³)	DRE test burn
Fenobucarb	<18	<21	>99.999997%
Fipronil	<12	<14	>99.999985%

Except for some temperature and NO_x fluctuations, no process upsets or disturbances occurred during the test burn. There is no requirement to demonstrate the combustion performance or to determine the destruction and removal efficiency by doing a test burns in Vietnam. The US Environmental Protection Agency regulation would require a DRE of 99.99% for these insecticides (Federal Register, 2000).

4.4.2Dioxins and furans

This was the first time dioxins and furans (PCDD/F's) were measured in an industrial facility in Vietnam. There is currently no emission limit value (ELV) for PCDD/F emissions from cement kilns in Vietnam, but hospital waste incinerators have an ELV of 1 ng I-TEQ/m³. The results of the dioxins and furans analysis are given in table 3. No international toxicity equivalents (I-TEQ) congeners were identified or quantified during the two days.

Table 3 ng I-TEQ PCDD/Fs/Nm³ (dry, 273K, 101.3kPa, 10% O₂)

<u>Congener</u>	<u>Baseline</u>	<u>Test burn</u>
2378 TCDF	<0.007	<0.010
2378 TCDD	<0.0034	<0.0051
12378 PeCDF	<0.0068	<0.010
23478 PeCDF	<0.0068	<0.012
12378 PeCDD	<0.0068	<0.010
123478 HxCDF	<0.0089	<0.013
123678 HxCDF	<0.0089	<0.013
234678 HxCDF	<0.0089	<0.013
123789 HxCDF	<0.0089	<0.013
123478 HxCDD	<0.0089	<0.013
123678 HxCDD	<0.0089	<0.013
123789 HxCDD	<0.0089	<0.013
1234678 HpCDF	<0.034	<0.051
1234789 HpCDF	<0.034	<0.051
1234678 HpCDD	<0.034	<0.051
OCDF	<0.17	<0.25

OCDD <0.17 <0.25

4.4.3 PAH's and HCB's

The results for PAH and HCB are given in table 4. Hexachlorobenzene (HCB) is currently not subject to regulatory monitoring in any cement plants but HCB monitoring may be a requirement under the Stockholm Convention in the future. HCB was below the detection limit both days. The results show that the emissions of PAH was very low and independent of co-processing of hazardous waste. There is no ELVs for PAH or HCB in Vietnam.

Table 4 Summary of results for PAH's and HCB (dry, 273K, 101.3kPa, 10% O₂)

	Baseline	Test burn
$\Sigma \mu\text{g PAHs/m}^3$	1.8	0.49
<u>ng HCB/m³</u>	<u>< 31</u>	<u>< 35</u>

Of the PAH's measured, only Fluorene, Phenanthrene and Fluoranthene was identified in low concentrations in the baseline test and only Phenanthrene was identified in low concentration during the test burn. Naphthalene could not be quantified in any of the samples as it was found to be contaminant in the XAD-2 resin.

Table 5 PAH congeners measured ($\mu\text{g/Nm}^3$)(dry, 273K, 101.3kPa, 10% O₂)

<u>PAH Congeners</u>	<u>Baseline</u>	<u>Test burn</u>
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Acenaphthylene	<0.17	<0.25
Acenaphthene	<0.17	<0.25
Fluorene	0.26	<0.25
Phenanthrene	1.36	0.49
Anthracene	<0.17	<0.25
Fluoranthene	0.20	<0.25
Pyrene	<0.17	<0.25
Benzo(a)anthracene	<0.17	<0.25
Chrysene	<0.17	<0.25
Benzo(b)fluoranthene	<0.17	<0.25
Benzo(k)fluoranthene	<0.17	<0.25
Benzo(e)pyrene	<0.17	<0.25
Benzo(a)pyrene	<0.17	<0.25
Perylene	<0.17	<0.25
Dibenz(ah)anthracene	<0.17	<0.25
Indeno(123cd)pyrene	<0.17	<0.25
<u>Benzo(ghi)perylene</u>	<u><0.17</u>	<u><0.25</u>
<u>Σ PAHs</u>	<u>1.8</u>	<u>0.49</u>

4.4.4 PCB's

All the Polychlorinated biphenyls (PCB's) sampled and analysed during the baseline and the test burn were below the detection limit. There is currently no emission limit value for PCB's in Vietnam. PCB's are not subject to regulatory

monitoring in any cement plants today but may be a requirement under the Stockholm Convention in the future.

Table 6 Dioxin like PCBs (ng/Nm³) (dry, 273K, 101.3kPa, 10% O₂)

<u>PCB Congeners</u>	<u>Baseline</u>	<u>Test burn</u>
<i>Non-ortho PCB's</i>		
3,3',4,4'-Tetrachlorobiphenyl	< 0.034	< 0.051
3,4,4',5-Tetrachlorobiphenyl	< 0.017	< 0.025
3,3',4,4',5-Pentachlorobiphenyl	< 0.009	< 0.013
3,3',4,4',5,5'-Hexabiphenyl	< 0.009	< 0.013
<i>Mono-ortho PCB's</i>		
2,3,3',4,4'-Pentachlorobiphenyl	< 0.170	< 0.254
2,3,4,4',5-Pentachlorobiphenyl	< 0.034	< 0.051
2,3',4,4',5-Pentachlorobiphenyl	< 0.341	< 0.507
2',3,4,4',5-Pentachlorobiphenyl	< 0.034	< 0.051
2,3,3',4,4',5-Hexabiphenyl	< 0.170	< 0.254
2,3,3',4,4',5'-Hexabiphenyl	< 0.034	< 0.051
2,3',4,4',5,5'-Hexabiphenyl	< 0.170	< 0.254
<u>2,3,3',4,4',5,5'-Heptabiphenyl</u>	<u>< 0.034</u>	<u>< 0.051</u>

4.4.4.1 Sampling and analysis

Sampling for Polychlorinated Dibenzo-p-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), Hexachlorobenzene (HCBS) and Fenobucarb and Fipronil was

performed in accordance with US EPA Method 23 (Federal Register, 2000). This method has been proven to be effective for the sampling of a wide range of semi-volatile organic compounds from combustion systems, including PCB's, PAH's, HCB's and pesticides. The XAD-2 resin was spiked prior to sampling with isotopically labelled PCDD/F's surrogate standards. In the laboratory, PCDD/F, PAH and PCB recovery standards were added to the sample components. The filter, resin and impinger solutions were extracted with organic solvents and the extract purified by chemical treatment and solid phase chromatographic techniques. Analysis of PCDD/F's was performed using high resolution gas chromatography with high resolution electron impact mass spectrometry in accordance with US EPA Method 1613A (Federal Register, 2000). The total toxic equivalent (TEQ) for each PCDD/F congener was calculated using international toxic equivalency factors (TEF's).

The method of extraction and purification of PAH's and PCB's are based on US EPA Methods 3540 (Soxhlet extraction of solid phase), 3510 (liquid/liquid extraction of aqueous phase), 3630 (SiO₂ gel column) and 3640 (GPC) (Federal Register, 2000). PAH's was analysed using high-resolution gas chromatography with low-resolution mass spectrometry. Analysis of PCB's was performed using high-resolution gas chromatography with high-resolution mass spectrometry. This method provides data for a selection of the most toxicologically significant "dioxin-like" PCB isomers. Toxic equivalents (TEQ's) are calculated for each of the targeted congeners using WHO 1998 (Federal Register, 2000). HCBs and insecticides were determined directly from the solid and liquid phase extracts (US EPA Methods 3540 and 3510) using high-resolution gas chromatography with low-resolution mass spectrometry (Federal Register, 2000).

4.4.5 Volatile Organic Compounds & Benzene

VOC and benzene was measured in the stack both days and were found in low concentrations, less than 4% and 13% of the current ELV respectively. Emissions of VOC and benzene are usually due to volatilisation of hydrocarbons in the raw materials when heated in the preheater and is normal in cement production.

Table 7 Benzene and VOC results (mg/Nm³) (dry, 273K, 101.3kPa, 10% O₂)

	Baseline	Test burn	ELV Vietnam
Benzene	2.2	3.2	80
VOCs	17	26	200

Sampling and analysis of VOC was performed in accordance with the US EPA Method 18 (Federal Register, 2000).

4.4.6 Hydrogen Chloride and Hydrogen Fluorides

Hydrogen fluoride and ammonia was measured to be below the detection limit both days and hydrogen chloride was well below the emission limit value. Even if the insecticide contained both chlorine and fluorine, the emissions were not affected.

Table 8 Hydrogen chloride, hydrogen fluoride and ammonia (mg/Nm³)

	Baseline	Test Burn	ELV
HCl	2.1	2.4	90
HF	<0.21	<0.23	4.5
NH ₃	<1.0	<0.44	45

Sampling and analysis was performed in accordance with US EPA Method 26A (Federal Register, 2000).

4.4.7 Carbon Monoxide and oxygen

The result for CO was well below the current emission limit value of 225 mg/Nm³ and independent of the insecticide co-processing.

Carbon monoxide can arise from any organic content in the raw materials and, occasionally, due to the incomplete combustion of fuel. The contribution from the raw materials, due to preheating, will be exhausted with the kiln gases. Control of CO levels is critical in cement kilns when electro static precipitators (ESP) are used for particulate abatement. If the level of CO in the ESP rises (typically to 0.5% by volume) then the ESP electrical system is automatically switched off to eliminate the risk of explosion.

The oxygen content measured during the test is within the normal range in cement kilns.

Table 9 Carbon monoxide (mg/Nm³) and oxygen (%)

	Baseline	Test burn	ELV
CO	99	131	225
O ₂	5.24	5.21	-

Oxygen and carbon dioxide concentrations were monitored in accordance with US EPA Method 3A and carbon monoxide in accordance with US EPA Method 10 (Federal Register, 2000).

4.4.8 Nitrogen and Sulphur Oxides

Table 10 shows the result of the nitrogen and sulphur oxides analysis. The result of SO₂ was less than 1% of the emission limit value (225 mg/Nm³) and independent of the insecticide co-processing. 99% of the sulphur oxides emitted from cement kilns is in the form of SO₂. SO₂ mainly originates from sulphides and organically bound sulphur in fuels and raw materials (Oss and Padovi, 2003).

The reason for the high NO_x levels during the test burn was due to high heat input through the main flame due to wrong information about heat content of the solvent of the insecticide prior to the test. The coal feed was approximately 1 ton higher than required; in addition, the insecticide contained nitrogen. The consequence of this inadequate compensation was higher temperature in the kiln and higher NO_x levels. However, the NO_x levels were higher than the ELV also under the baseline measurements. The result confirms what most studies have concluded with earlier, that more than 90% of the NO_x emissions from cement kilns are NO, the rest is NO₂.

Table 10 Nitrogen and sulphur oxides (mg/Nm³)

	Baseline	Test burn	ELV
SO ₂	1.8	2.0	225
NO ₂	21	40	-
NO	760	1220	-

NO_x expressed as NO₂ 1180 1910 1,000

NO and NO₂ concentrations were monitored in accordance with US EPA Method 7E and sulphur dioxide concentrations in accordance with US EPA Method 6C (Federal Register, 2000).

4.4.9 Total Solid Particles

The concentration of dust was 33 and 20 mg/Nm³ for the baseline test and the test burn respectively, i.e. independent of the insecticide co-processing. The ELV in Vietnam is 100 mg/Nm³. Sampling of solid particles was conducted in accordance with US EPA Method 5 (Federal Register, 2000).

4.4.10 Metals

The analysis results of Arsenic, Cadmium, Cobalt, Chromium, Copper, Mercury, Manganese, Nickel, Lead, Antimony, Tin, Thallium, Vanadium and Zinc are given in table 11. Vietnamese ELV's are given for Arsenic, Cadmium, Copper, Lead, Antimony and Zinc and all the results are in compliance.

The sources of heavy metals to a cement kiln are raw materials and fuels and will be site specific. The emission levels uncovered in this test are low and not influenced by insecticide co-processing. The results of tin are probably due to contamination or interferences in the analytical technique used in the laboratory.

Table 11 Heavy Metal Concentration in $\mu\text{g}/\text{Nm}^3$

	Baseline	Test Burn	ELV
As	<5.4	<2.7	4,500
Cd	0.71	0.74	450
Co	<0.54	<0.27	
Cr	1.7	4.3	
Cu	<1.1	0.71	9,000
Hg	4.7	0.33	
Mn	12	14	
Ni	1.6	1.8	
Pb	<4.3	<2.2	4,500
Sb	<3.3	<1.6	11,250
Sn	71	38	
Tl	<2.7	<1.4	
V	<0.65	0.82	
Zn	13	2.7	13,500

Monitoring of metals was performed in accordance with US EPA Method 29 (Federal Register, 2000). Hg was analysed by cold vapour atomic absorption spectroscopy (CV-AAS), the other metals by using inductively coupled argon plasma emission spectroscopy - mass spectrometry (ICP-MS).

4.4.11 Solid samples

Raw meal, clinker, fine coal, electro static precipitator dusts were sampled every second hour during the two days and analysed for main and trace inorganic components. The results showed no effect of hazardous waste co-processing. The results of chlorine and fluorine in clinker are showed in table 12. All the dusts produced by the ESP's are recovered and reintroduced in the process, i.e. no residues or waste is produced.

Table 12 Chlorine and fluorine in clinker (mg/kg; average value)

	<u>Baseline</u>	<u>Test burn</u>
Cl	18	19
F	<0.40	<0.40

4.4.12 Product quality

Ordinary quality testing was performed on clinker, cement and concrete produced the two days and comprised fineness of the cement, loss of ignition, water demand, initial and final setting time and the strength of the concrete after 1 day, 3 days, 7 days and 28 days. The results were within normal ranges and showed that the product quality was unaffected by the introduction of the insecticide.

5. Discussion

Vietnam is currently lacking sufficient treatment options for large quantities of hazardous waste. Thousands of industrial enterprises produce huge amounts of

hazardous wastes without having sufficient environmentally sound treatment or disposal options available. Some responsible enterprises store their wastes, waiting for options to become available; others don't know about the dangers of letting these wastes enter rivers and land. This situation is a treat to environment, health and to the economic development and needs to be dealt with in a responsible way.

Vietnam has an adequate regulation on hazardous waste management in place but the enforcement is weak. The main reason for this is that it's difficult to enforce when there are no adequate treatment options available. Basic treatment facilities needed is a combustion option for organic hazardous wastes, a physical-chemical treatment option for inorganic hazardous wastes and a secure landfill for residues which can't be recovered or treated further.

Many countries are using cement kilns to treat organic hazardous wastes, in Norway this is the only option available. Cement kilns have been used for more than 20 years and shown to be beneficial both for society and the cement industry. The cement industry uses huge amounts of non-renewable fossil fuels and raw materials and the only way forward to become more sustainable is to replace these with waste materials.

The modern Holcim preheater/precalciner cement kiln in Hon Chong possess many inherent features which makes it ideal for hazardous waste treatment; high temperatures, long residence time, surplus oxygen, good mixing conditions, thermal inertia, counter currently dry scrubbing of the exit gases by alkaline raw material and no waste or residues to dispose of. These inherent features actually makes a test burn redundant, however, a test burn is the only way to prove the destruction capabilities of a particular kiln and will add trust to professionals and lay people. The EU regulation doesn't require a test burn, only compliance with emission limit values.

A dedicated hazardous waste incinerator with the same features would imply huge investments and high running costs, and it's questionable if such investment is justifiable. The willingness and capability of Vietnamese industry to pay for adequate hazardous waste treatment is uncertain, especially because the enforcement is weak. International companies would be willing to pay for sound treatment options, but it's questionable if this is enough to have a sufficient payback. If the treatment options are too expensive, many industries will continue to use the cheapest option, the rivers.

The Holcim cement plant and its infrastructure are in place and ready to start to substitute some of its non-renewable materials with wastes. The test burn followed a modified verification scheme, applying National requirements together with the best of the EU and the US regulation and clearly demonstrated the suitability of the cement kiln to co-process organic hazardous wastes in an environmentally sound manner. Instead of representing a threat to environment and health, and causing a headache of the owner, the toxic and dangerous insecticide was safely destroyed at the same time as it was beneficially used to replace a considerable amount of non-renewable fossil fuel, more than 10% of the heat requirement.

The kiln constitutes the best available techniques and best environmental practice (BAT/BEP) and the only questions which remained unanswered were the destruction performance of stable organic hazardous constituents and the emissions of POP's. No process upsets or disturbances occurred during the test burn with the insecticide. The destruction and removal efficiency was measured to be close to "8-nines" and compared with the most stringent regulatory requirements in the world today, the US, the result was almost "10,000 times better". Except for the NO_x emissions, the test result was in compliance with most stringent international regulations.

The reason for the high NO_x levels during the test burn was due to high heat input through the main flame due to wrong information about heat content of the solvent of the insecticide prior to the test. The coal feed was approximately 1 ton higher than required. The consequence of this inadequate compensation was higher temperature in the kiln and higher NO_x levels. The “easy burnability” of the solvent of the insecticide compared to hard coal probably caused a more intense flame in the main burner as well as added 31 kg of nitrogen per hour. There is mainly three types of NO_x generated in cement production, thermal NO_x which is due to the high temperature, and fuel and raw material NO_x , which is due to release of NO_x from the two inputs. The NO_x generation in cement kilns consists mainly of NO which is formed at temperatures above $1,200^\circ\text{C}$ and increases markedly above $1,400^\circ\text{C}$ (Oss and Padovani, 2003). Thermal NO_x dominates over fuel NO_x in the main burner flame in the kiln. In the secondary firing of the precalciner with a flame temperature below $1,200^\circ\text{C}$, the formation of thermal NO_x is much lower compared to the main burner flame; hence fuel NO_x is generated primarily in the precalciner (Oss and Padovani, 2003).

NO_x formation increases with the amount of excess air in the flame and decreases in reducing atmospheres with low oxygen. When operating near to stoichiometric conditions in the kiln, localized generation of carbon monoxide will convert any NO to nitrogen. The formation of NO_x in cement kilns is complex and as yet incompletely understood. Most studies have concluded that more than 90% of the NO_x emissions from cement kilns are NO, the rest NO_2 ; almost no nitrous oxide (N_2O) is formed in cement kilns. Thermal NO_x usually makes up 70% or more of the total NO_x and is formed by direct oxidation of atmospheric nitrogen through the dissociation of O_2 and N_2 . Thermal NO_x begins to form at temperatures as low as

1200°C and increases rapidly with even small temperature increases when within the range of 1370°C to 1870°C; the high-end temperature approximates that of the gas temperatures in the kiln's sintering zone. Given the high kiln temperatures, even small shifts in the amount of combustion oxygen can have a pronounced effect on the amount of thermal NO_x formed. Wastes used in cement kiln co-processing normally have slightly lower heat content than normal coal and can even be used for NO_x control. The result confirms what most studies have concluded with earlier, that more than 90% of the NO_x emissions from cement kilns are NO, the rest is NO₂.

There are many ways to abate and control NO_x emissions by primary measures and optimization, including process control, improved firing techniques, optimized cooler connections, fuel selection, air optimization regimes (control ambient air infiltration), raw material proportioning and blending, use of waste material to achieve flame cooling in the sintering zone, staged combustion and reducing conditions (Oss and Padovani, 2002).

Due to the availability of a good performing cement kiln Vietnam may be able to forego the need to invest in costly, and controversial, hazardous waste treatment options like rotary kiln incinerators. The co-processing option will enable the authorities to strengthen the environmental laws and to enforce the hazardous waste management regulation. All generators, transporters, or owners of hazardous waste pollution, including national, state, and local government entities, should be held to the same compliance standards and subject to the same enforcement practices. When wastes from one industry are used and recovered beneficially by another industry we have a true cost-effective and sustainable solution, at the same time as serious environmental problem and potential health are omitted. As in Norway in the 1980's, this constitutes a tremendous opportunity for Vietnam.

Conclusion

Large amounts of hazardous chemicals and wastes constitute a serious threat to health and environment in many developing countries and Vietnam is no exception. In the Southern Focus Economic Zone of Vietnam more than 30,000 industrial enterprises produces approximately more than 73,000 tonnes of hazardous wastes yearly, without having any environmentally sound treatment or disposal options available.

The advantages of high temperature cement kilns are widely utilised around the world for fossil fuel substitution and raw material recovery. A test burn was conducted in a modern cement kiln in South Vietnam to investigate the feasibility of co-processing of organic hazardous waste by doing a one-run test burn with a toxic and dangerous insecticide under normal operating conditions. The test burn demonstrated the suitability of the cement kiln to co-process hazardous wastes in an irreversible and environmental sound manner and that a controlled substitution of fossil fuel with hazardous waste doesn't affect the emissions.

This was the first time PCDD/F's, PCB's and Hexachlorobenzene was measured in an industrial facility in Vietnam and all the results were below the detection limits. This clearly proved that the destruction was complete and irreversible, and thereby in full compliance with the requirements of the newly ratified Stockholm Convention.

The co-processing option is made available through private investments and can immediately be used to treat a considerable amount of the 73,000 tons of hazardous wastes generated each year in South Vietnam. This will be beneficial for

the health of the people, for the environment and for sustainable economic growth in the region.

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