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## Review

# Environmentally sound destruction of obsolete pesticides in developing countries using cement kilns

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## ABSTRACT

The accumulation and inadequate management of obsolete pesticides and other hazardous chemicals constitutes a threat for health and environment, locally, regionally and globally. Estimates indicate that more than 500,000 tonnes of obsolete pesticides are accumulated globally, especially in developing countries. FAO has been addressing this issue and disposed of approximately 3000 tonnes of obsolete pesticides in Africa and the Near East since the beginning of the 1990s. These pesticide wastes have mainly been shipped to Europe for high-temperature combustion in dedicated incinerators, a treatment option usually not available in developing countries.

High temperature cement kilns are however commonly available in most countries and have shown to constitute an affordable, environmentally sound and sustainable treatment option for many hazardous chemicals if adequate procedures are implemented. Cement kilns have been used for disposal of obsolete pesticides in developing countries earlier but no study has been able to verify the destruction efficiency in an unambiguous way. Lessons learned from earlier experiences were used to carry out a test burn with two obsolete insecticides in a cement kiln in Vietnam. The destruction efficiency was measured to be better than 99.999969% for Fenobucarb and better than 99.999832% for Fipronil and demonstrated that the hazardous chemicals had been destroyed in an irreversible and environmental sound manner without new formation of dioxins, furans, hexachlorobenzene or PCBs, a requirement of the Stockholm Convention on POPs.

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## 1. Introduction

The accumulation and inadequate management of obsolete pesticides and other hazardous chemicals constitute a threat to health and environment, locally, regionally and globally. Estimates indicate that more than 500,000 tonnes of obsolete pesticides are accumulated globally, especially in developing countries (FAO, 2001a). FAO has been addressing this issue and disposed of approximately 3000 tonnes in more than ten countries in Africa and the Near East since the beginning of the 1990s (FAO, 2001b), less than 1% of the existing stocks.

A considerable amount of the accumulated obsolete pesticides are persistent organic pollutants (POPs) that possess toxic properties, resist degradation, bio-accumulate and are transported, through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems (Vallack et al., 1998; Jones and de Voogt, 1999). Organochlorine pesticide residues have been detected in air, water, soil, sediment, fish, and birds globally even more than one decade after being banned and it's reasonable to believe that contaminated sites and stockpiled waste still represent locally and regionally important on-going primary source inputs of hazardous compounds to the global environment (Brevik et al., 2004).

The Arctic, where subsistence living is common, is a sink region for POPs. Norwegian and Canadian researchers find more POPs in Polar bear on the remote North Atlantic island Svalbard than on the mainland America and there is currently a great concern in Norway about a 5–10 times increase in the POPs concentration in fish and other animals in the Barents Sea the last 10–15 years (Gabrielsen et al., 2004). POPs have shown to interfere with hormone function and genetic regulation, and myriad dysfunctions can be induced by low-dose POPs exposure during development (De Vito and Birnbaum, 1995; McDonal, 2002; Godduhn and Duffy, 2003; WHO, 2003; Gupta, 2004; Jobling et al., 2004).

Several international conventions aim to protect human health and the environment by requiring Parties to take measures to reduce or eliminate releases of POPs from intentional production and use, from stockpiles and wastes and from unintentional release. The Aarhus Protocol (UNECE, 1998) covers 16 POPs, 11 of which are pesticides, which are aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene (HCB), mirex, chlordecone, lindane, and toxaphene. The Stockholm Convention on POPs (UNEP, 2001) covers for the time being 12 compounds or groups of compounds, which are polychlorinated biphenyls (PCB), polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) and 9 of the same pesticides as the Aarhus Protocol, except chlordecone and lindane.

There is currently no reliable information available of what quantities these POPs constitute on a global level but these conventions acknowledge that there is an urgent need for environmentally sound disposal and that developing countries and countries with economies in transition need to strengthen their national capabilities on sound management of hazardous chemicals (UNEP, 2001). One of the intentions of the Basel Convention on the Control of Transboundary Movement of Hazardous Wastes is to stimulate local treat-

ment of hazardous wastes and to avoid shipment across borders (Basel Convention, 1989).

Pesticide wastes from clean up in Africa have so far been shipped to Europe for high-temperature combustion in dedicated incinerators at an average cost of US\$ 3500 per tonnes (FAO, 1999; Science in Africa, 2002). Apart from being costly, this practise also involves environmental risks due to long transport distances and it does not contribute with needed capacity building on hazardous waste management in the affected countries. High temperature incineration is usually absent as a dedicated technology option in developing countries but high temperature cement kilns are however common in most countries and can constitute an affordable, environmentally sound and sustainable treatment alternative to export (Karstensen, 1998a,b, 2001a,b, 2004). The only treatment option for organic hazardous wastes in Norway the last 25 years has been co-processing in cement kilns (Viken and Waage, 1983; Benestad, 1989; Karstensen, 1998a).

The Stockholm Convention has mandated the Basel Convention (2006) to develop technical guidelines for environmentally sound management of wastes consisting of or contaminated with POPs. An important criterion for environmentally sound destruction and irreversible transformation is to achieve a sufficient destruction efficiency (DE) or destruction and removal efficiency (DRE). A DRE value greater than 99.9999% is required for POPs in the United States (US) (Federal Register, 1999). The DRE consider emissions to air only while the more comprehensive DE is also taking into account all other out-streams, i.e. products and liquid and solid residues.

The Basel Convention technical guidelines consider ten technologies to be suitable for environmentally sound destruction/disposal of POPs (Basel Convention, 2006). The most common among these are hazardous waste incineration and cement kilns, which also constitute the largest disposal capacity. The remaining eight technologies have comparatively low capacities (some are still at laboratory scale), are technically sophisticated and currently not affordable by many developing countries (UNEP, 2004). A thorough and objective comparison between these technologies on aspects like sustainability, suitability, destruction performance, robustness, cost-efficiency, patent restrictions (availability), competence requirements and capacities is needed.

## 2. Cement production and co-processing of hazardous wastes

Portland cement is made by heating a mixture of calcareous and argillaceous materials to a temperature of about 1450 °C. In this process, partial fusion occurs and nodules of so-called clinker are formed. The cooled clinker is mixed with a few percent of gypsum, and sometimes other cementitious materials, and ground into a fine meal—cement (Duda, 1985; IPCC, 2001). In the clinker burning process, which is primarily done in rotary kilns, it is essential to maintain kiln charge temperatures of approximately 1450 °C and gas temperatures in the main flame of about 2000 °C. The cement industry is today widely distributed throughout the world and produced in 2003 approximately 1940 million tonnes of

cement (Cembureau, 2004). When new plants are built in emerging markets and developing countries, usually the best available techniques (BAT) applies (IPPC, 2001; Karstensen, 2006b).

Cement kilns have proven to be effective means of recovering value from waste materials and co-processing in cement kilns is now an integral component in the spectrum of viable options for treating hazardous industrial wastes, mainly practised in developed countries (Balbo et al., 1998). A cement kiln possess many inherent features which makes it ideal for hazardous waste treatment; high temperatures, long residence time up to eight seconds, surplus oxygen during and after combustion, good turbulence and mixing conditions, thermal inertia, counter currently dry scrubbing of the exit gas by alkaline raw material (neutralises acid gases like hydrogen chloride), fixation of the traces of heavy metals in the clinker structure, no production of by-products such as slag, ashes or liquid residues and complete recovery of energy and raw material components in the waste (Chadbourne, 1997).

Numerous tests in developed countries have demonstrated that there is essentially no difference in the emissions or the product quality when waste materials are used to replace the fuels and ingredients needed to produce cement clinker (Lauber, 1982, 1987; Branscome et al., 1985; Garg, 1990; Karstensen, 1994; Chadbourne, 1997). Mac Donald et al. (1977) carried out test burns with hazardous chlorinated hydrocarbons containing up to 46% chlorine in a wet cement kiln in Canada and concluded that “all starting materials, including 50% PCBs, were completely destroyed” and “that all chlorinated hydrocarbon wastes may be used in cement kilns without adverse effect on air pollution levels”. Similar tests with chlorinated and fluorinated hydrocarbons conducted in a wet kiln in Sweden showed that the DRE of PCBs were better than 99.99998% and that there were no change in product quality or any influence on process conditions with a chlorine input up to 0.7% of the clinker production (Ahling, 1979). Viken and Waage (1983) carried out test burns in a wet kiln in Norway feeding 50 kg PCBs per hour, showing a DRE better than 99.9999% and no traces of PCB in clinker or dusts could be detected. Benestad (1989) carried out studies in a dry cement kiln in Norway in 1983 and 1987 and concluded that “the type of hazardous waste used as a co-fuel does not influence the emissions” and that the destruction of PCB was better than 99.9999%. Suderman and Nisbet (1992) concluded from a study in Canada that there is “no significant difference in stack emissions when 20–40% of the conventional fuel is replaced by liquid wastes”.

### 3. Disposal of obsolete pesticides and POPs in developing countries using cement kilns—lessons learned

Despite the obvious need, surprisingly few studies have reported results from obsolete pesticide and POPs destruction using cement kilns in developing countries.

#### 3.1. Malaysia

The German development aid organisation GTZ carried out the first reported disposal operation with obsolete pesticides

using a cement kiln in Malaysia in the middle of the 1980s (Schimpf, 1990). Solid and concentrated liquid pesticides were dissolved in kerosene and fuel oil in a 5 m<sup>3</sup> storage tank with an agitator and fed through the main burner into the kiln. A mixture of 2,4-D and 2,4,5-T were destroyed in the main flame of the kiln. Before, during and after the disposal, dust samples were taken from the electro static precipitator (ESP) and analysed for PCDD/Fs. No PCDD/Fs were detected, but the report does not provide any information of the quantification limits for PCDD/Fs, nor any information about the amounts of pesticides destroyed, the concentration of the active ingredients, the feed rate into the kiln or the DE/DRE.

#### 3.2. Pakistan

A total of 17,000 l of nine different organophosphates and three different organochlorine pesticide mixtures were destroyed in a cement kiln in Pakistan by the US Aid in 1987 (Huden, 1990). Waste pesticides were pumped from a tank truck and injected at an average rate of 294 l/h for the organophosphates and 46 l/h for the organochlorines. The injector achieved fine atomisation using compressed air and was tested successfully with diesel fuel. The “cocktail” of pesticides, however, contained sludge’s that settled to the bottom of the tank truck, causing viscosity to fluctuate depending on temperature and degree of agitation. These unanticipated conditions caused a variety of problems. The kiln met the standards for dust emission but not the DRE requirement or the HCl emissions limit. Products of incomplete combustion (PIC) were examined using gas chromatography mass spectrometry (GC-MS) but were not detected. Analyses of solid process samples, raw meal feed, and clinker and ESP dust showed no detectable pesticides.

#### 3.3. Tanzania

Mismanagement of large quantities of 4,6-dinitro-*o*-cresol (DNOC) during several years in the 1980s and 1990s caused serious environmental and ecological damages to the wildlife in Lake Rukwe in west Tanzania. DNOC belongs to the group of nitro-compounds and is classified to be highly hazardous (group Ib) in accordance to the WHO (2002) classification and is highly toxic to fish and explosive in its dry form. GTZ carried out a test burn with 1:1 DNOC/diesel-mixture in a cement kiln west of Dar-Es-Salaam in 1996 (Schimpf, 1998). A series of technical problems led to delays, especially during the testing phase and the composition of the exit gas concentration of CO, CO<sub>2</sub>, O<sub>2</sub>, NO<sub>x</sub> and the temperature fluctuated during the test burn but no DNOC residues were detected in the clinker or the filter dust. Approximately 57,500 l of 20% DNOC were co-processed in the kiln within a period of about 7 weeks. The 400 old DNOC drums were melted and recycled as iron for construction purposes. The cost of the disposal was estimated to be approximately 4300 US\$ per tonne of DNOC, a cost lying in the “upper range of normal disposal costs” according to Schimpf (1998). This way of calculating the disposal cost seems however to be dubious—the total project cost, 245,000 US\$ over 4 years, is divided on the 57 tonnes of pesticides disposed.

### 3.4. Poland

In a Polish test burn reported by Stobiecki et al. (2003) different mixes of 12 obsolete pesticides and POPs were introduced into a cement kiln (no details about the process type or operating conditions) over a period of 3 days. The different pesticide mixtures were blended into three batches with light heating oil and constituted 11.5%, 29.4% and 30.5% of pesticides, respectively. The mixes were fed through the main flame together with the coal in an introduction rate of approximately 400 kg/h over three different periods and the results was compared to baseline conditions, i.e. when coal only was used as a fuel. None of the pesticides were detected in the exit gas (detection limit between 1 and 0.02  $\mu\text{g}/\text{m}^3$ ) or in the clinker (detection limit between 0.05 and 0.001 mg/kg). Physical and chemical testing of clinker gave normal and similar results for all conditions. The PCDD/Fs emissions were 0.009 ng I-TEQ/ $\text{N m}^3$  with coal only and 0.015, 0.053 and 0.068 ng I-TEQ/ $\text{N m}^3$  when feeding the three fuel mixes with pesticides, respectively.

### 3.5. Lessons learned

None of the described projects were able to demonstrate the destruction efficiency, an important criterion for the evaluation of environmentally sound destruction/disposal (Basel Convention, 2006), but also important for achieving acceptance for this treatment option among various stakeholders.

The absence of PCDD/Fs in the ESP dust in the GTZ project in Malaysia is not enough to verify the destruction performance, nor did it provide information of the quantification limits for PCDD/Fs. There is however no reason to believe that 2,4-D and 2,4,5-T were not safely destroyed in the main flame but the DE/DRE should have been established.

For the purpose of the test burn in Pakistan it might have been wise to insist on using a uniform, higher grade waste pesticide and restricting the test to one compound in each pesticide group. Uncertainty of availability of the ideal test candidate, likely long haul transport, and need to get on with the job, forced the team into a truly real case waste disposal situation, the complexity of which did not become apparent until they were well committed and could not turn back (Huden, 1990). Better early sampling of candidate pesticides could have told the team more of what was ahead as well as determined a better choice of pesticides for the test burn. The choice of laboratory is of course also important. The concentration of pesticides in the feed was too low to measure the DE/DRE, probably due to a combination of low active ingredient and low feed rate. Further on, in selecting a cement plant for waste co-processing, the power supply reliability is essential. The actual plant was plagued by many power interruptions. When designing the waste injection and delivery system, the team expected to work with free flowing liquids but received sludge which caused numerous problems. The waste products should have been blended in a dedicated tank, equipped with an agitator and fed to the fuel line equipped with a cut-off valve. The important public relations issue was according to Huden (1990) not given enough attention. To assume that a potentially touchy subject best

be kept quiet, is dangerously naive. The press, community leaders and labour unions can quickly turn into enemies when they are not informed of the intent of such an undertaking. With proper care, popular acceptance is much more likely than not, particularly when the benefit of participating in risk reduction can be understood.

The kiln chosen for the disposal operation of DNOC in Tanzania (Schimpf, 1990) was obviously not the best choice and illustrates clearly the necessity of performing a proper technical feasibility study prior to the kiln selection. The kiln broke down regularly during the disposal operation, the refractory of the kiln was damaged, the outer wall of the satellite cooler burned through, the power fluctuated and the raw meal feed was disrupted. There was no sampling of DNOC in the exit gas, i.e. no possibility to demonstrate the DE/DRE. To measure DNOC in ESP dust and clinker, and  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{NO}_x$  in the exit gas is not sufficient. The project experienced resistance from the plant employees and showed clearly the necessity of transparency, information and good communication with involved parties.

Stobiecki et al. (2003) analysed the stack gas and the clinker for the 12 obsolete pesticides fed to the kiln but did not, for unknown reasons, report the DE/DRE.

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## 4. Test burn with obsolete pesticides in a Vietnamese cement kiln

Lessons learned from the described projects established the basis for a joint test burn project with the Vietnamese authorities and Holcim Cement Company. The objective was to investigate if their cement kiln in the South of Vietnam was able to co-process and destroy obsolete pesticides/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. Information about the test burn was disseminated well in advance to all relevant stakeholders and the actual test burn was inspected by scientists from universities and research institutes in Vietnam. Several conditions had to be fulfilled prior to the test burn:

- Project supervision and evaluation by third party experts.
- Independent stack gas sampling and analysis by an accredited company.
- An environmental impact assessment (EIA) following the Vietnamese requirements had been successfully completed (Decision 155, 1999; HCMC, 2002).
- The transport and the handling of the hazardous waste should comply with the hazardous waste management regulation in Vietnam, Decision 155 (1999).
- The emission levels should comply with the Vietnamese emission limit values in the standard TCVN 5939-1995 and TCVN 5940-1995 (Decision 155, 1999; Karstensen et al., 2003a).
- The cement kiln process had been evaluated to be technical and chemical feasible for co-processing of hazardous wastes.
- Power and water supply had been evaluated to be stable and adequate.

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

#### 4.1. Cement plant description

The 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 new dry suspension preheater rotary cement kiln equipped with a precalciner, a best available techniques plant (IPPC, 2001). The kiln rotates with a speed of 3.5 rounds per minute, is 4.6 m in diameter, 72 m long with a 110 m high double string five-stage preheater tower and produces approximately 4400 tonnes of clinker per day.

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 by-pass system to reduce build-up of chlorine and alkalis if needed. After drying, the gas is de-dusted in high efficiency 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, O<sub>2</sub>, CO and NO<sub>x</sub>; the preheater outlet gas for temperature, O<sub>2</sub>, CO and NO<sub>x</sub> and the stack outlet gas for temperature, O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub>, HCl, NH<sub>3</sub>, H<sub>2</sub>O and volatile organic carbon (VOC). The main stack is 122 m high and approximately 4 m in diameter.

#### 4.2. Obsolete pesticides used in the test burn

The greatest challenge in the first phase of the project was to identify a local available obsolete pesticide which could fit the purpose of being a suitable test burn candidate and avoid the trouble Huden (1990) faced in Pakistan.

A solvent-based insecticide mix with two active ingredients, 18.8% Fenobucarb and 2.4% Fipronil, was identified at an international pesticide company in Dong Nai Province. The insecticide had expired, was deemed unusable and approximately 40,000 l was stored in 200 steel drums waiting for a suitable treatment option. The active ingredients of the insecticide were solved in cyclohexanone and aromatic solvents. The concentration was regarded to be sufficient to be able to demonstrate the necessary DE/DRE of 99.99%. Fenobucarb has a molecular weight of 207.3 with the sum molecular formula C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub> (Fig. 1).

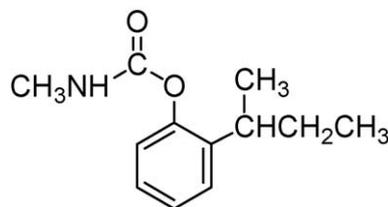


Fig. 1 – Chemical structure of Fenobucarb.

Fipronil has a molecular weight of 437.2 with the sum molecular formula C<sub>12</sub>H<sub>4</sub>Cl<sub>2</sub>F<sub>6</sub>N<sub>4</sub>OS and contain 16.2% chlorine and 26.06% fluorine (Fig. 2). Fenobucarb and Fipronil contain 6.7% and 12.8% nitrogen, respectively.

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 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 insecticides were also considered to be representative of other obsolete pesticide and hazardous waste streams needing a treatment option in Vietnam and would as such constitute an illustrative example (Quyen et al., 1995; DoSTE, 1998; Hung and Thiemann, 2002; Karstensen et al., 2003a,b; Minh et al., 2004; World Bank, 2004). The other requirement, which was based on the lessons learned from the earlier studies, was the need of having sufficient amounts and concentration of a homogeneous compound.

The insecticide mix was a free flowing liquid with a viscosity similar to water and easy to pump through a separate channel in the main burner, a three channel burner feeding anthracite coal only under normal operations. The product had been screened through 0.25 mm sieve and no settlements, particles or polymerization or degradation of the active ingredient were observed. The Plant Protection Department in Ho Chi Minh City confirmed that the product was homogenous and contained 18.8% Fenobucarb and 2.4% Fipronil. Quantitative and qualitative analysis is usually done by high pressure liquid chromatography with ultra violet detection or by gas chromatography with electron capture detection (Kawata et al., 1995; Vilchez et al., 2001).

A 16 m<sup>3</sup> steel tank for receiving, blending and feeding of the insecticide mix was built and 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 and was placed in a bunded concrete construction for spill recovery. The insecticide mix was pumped from the tank through stainless steel pipes

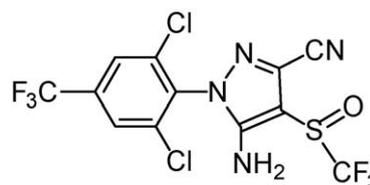


Fig. 2 – Chemical structure of Fipronil.

through a calibrated flow meter and into the main flame together with coal.

The transport of the 200 steel drums with insecticide was carried out by 10 trucks and organised by the owner. The emptying of the insecticide drums were done manually with a steel lance, chemical resistant hose and a diaphragm pump connected directly to the feeding tank and 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. 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 2 days, 16 and 17 October 2003, starting first day with a baseline study with coal feeding only and then the test burn the second day were parts of the coal was substituted by the insecticide mix. The plant was run both days in a normal mode, i.e. with the kiln gases directed through the raw mill for drying purpose.

The sampling of solid process samples, i.e. raw meal, clinker, fine coal, and dust from the ESP was carried out by trained plant staff. An Australian independent test company accredited according to EN ISO/IEC 17025 was hired to carry out the stack gas sampling. They subcontracted other accredited laboratories in Australia and Europe to do the chemical analysis.

The insecticide mix was introduced to the kiln starting with 1000 l per hour (l/h), increasing to 2000 l/h 6 h before the stack sampling started in order to stabilise test conditions. During the stack sampling campaign, 2030 l of insecticide mix was fed to the kiln per hour and all together 39,500 l were destroyed in less than 20 h. After emptying, tank and pipes were cleaned with light fuel oil and fed to the kiln.

#### 4.4. Process and sampling conditions during testing

Two hundred and ninety-two tonnes per hour of raw meal was fed to the preheater and 179 tonnes/h of clinker was produced during the test. Feeding of coal to the secondary precalciner burner was stable at 13 tonnes/h both days; the coal feed to the main primary burner was reduced by 1.5 tonnes from 7 to 5.5 tonnes/h when the insecticide mix was introduced to compensate for the heat input of the solvent.

The coal feed to the main burner was not reduced sufficiently during the test burn due to an analysis error of the heat content of the insecticide mix. Measurements prior to the test had shown a calorific value of 22.5 MJ 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 mix was measured to be 36.6–38.1 MJ/kg (due to the aromatic solvents). Fine coal is by comparison 30 MJ/kg, i.e. the coal feed to the main burner should have been reduced by 2.5 tonnes to balance the heat requirement of the kiln.

#### 4.5. Emissions results and discussion

##### 4.5.1. Destruction efficiency of the insecticides

To make sure that Fenobucarb and Fipronil was not a PIC normally found in the stack emissions, Fenobucarb and Fipronil were also analysed in the samples taken during the baseline test. Both DE and DRE were measured during the test. The DE is calculated on the basis of mass of the insecticide fed to the kiln, minus the mass of the remaining insecticide in the stack emissions, in the clinker and the ESP dust, divided by the mass of the insecticide within the feed, according to the following equation:

$$DE = \frac{W_{in} - W_{out}}{W_{in}} \times 100$$

where  $W_{in}$  is the mass of Fenobucarb and Fipronil entering the kiln and  $W_{out}$  is the mass exiting the stack gas and through the clinker and ESP dust. The actual cement plant does not produce any liquid effluents. The DRE considers emissions to air only.

The introduction of 2030 l/h insecticide 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 clinker, the ESP dusts (the detection limit was 2 ng/g) or in the exit gas (the detection limit was 21 and 14 ng/m<sup>3</sup>, respectively). The DE/DRE is calculated on the basis of the material volumes produced and an average stack gas volume of 484,800 normal cubic metre per hour (N m<sup>3</sup>/h) corrected to 10% oxygen (Table 1).

The US EPA regulation would require a DRE of 99.99% for these insecticides; no DE demonstration is however required (Federal Register, 1999). There is no requirement for demonstrating the DE/DRE in the Vietnamese regulation.

##### 4.5.2. Result of organic compounds

Sampling for PCDD/Fs, PCBs, and polyaromatic hydrocarbons (PAHs), HCB, 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 PCBs, PAHs, HCB and pesticides. The XAD-2 resin was spiked prior to sampling with isotopically labelled PCDD/Fs 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/Fs was performed using high-resolution gas chromatography with high resolution mass spectrometry in accordance with US EPA

**Table 1 – Fenobucarb and Fipronil in the stack (ng/m<sup>3</sup>)**

	Baseline	Test burn	DRE test burn (%)	DE test burn (%)
Fenobucarb	<18	<21	>99.999997	>99.9999969
Fipronil	<12	<14	>99.999985	>99.9999832
Calculated DE and DRE.				

Method 8190 (Federal Register, 2000). The total toxic equivalents (TEQs) for 2,3,7,8-substituted PCDD/F congeners were calculated using international toxic equivalency factors (TEFs).

The method of extraction and purification of PAHs and PCBs are based on US EPA Methods 3540 (Soxhlet extraction of solid phase), 3510 (liquid/liquid extraction of aqueous phase), 3630 (SiO<sub>2</sub> gel column) and 3640 (GPC) (Federal Register, 2000). PAHs were analysed using high-resolution gas chromatography with low-resolution mass spectrometry. Analysis of PCBs was performed using high-resolution gas chromatography with high-resolution mass spectrometry determining “dioxin-like” PCB congeners with the TEF scheme provided by WHO 1998 (Federal Register, 2000). HCB and the 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). Sampling and analysis of VOC was performed in accordance with the US EPA Method 18 (Federal Register, 2000).

This was the first time PCDD/Fs were measured in an industrial facility in Vietnam. There is currently no PCDD/F emission limit value for cement kilns but hospital waste incinerators have an ELV of 1 ng I-TEQ/N m<sup>3</sup>. No 2,3,7,8-substituted PCDD/Fs could be quantified.

HCB is currently not subject to common regulatory monitoring in cement plants but may be a requirement under the Stockholm Convention in the future. HCB was below the detection limit both days. The PAH emission was low and independent of the insecticide disposal. There is currently no ELV for PAH or HCB in Vietnam (Table 2).

VOC and benzene were 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.

Of the PAHs measured, only fluorene, phenanthrene and fluoranthene were 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 a contaminant in the XAD-2 resin.

All the dioxin-like PCBs was below the detection limit. There is currently no ELV for PCBs in Vietnam. PCBs are not commonly monitored on a regular basis in cement plants but will be a requirement under the Stockholm Convention in the future.

#### 4.5.3. Result of acids and gases

Hydrogen fluoride and ammonia were measured to be below the detection limit both days and hydrogen chloride was well

**Table 2 – Concentration of PAH, HCB, benzene and VOC (dry gas at 273 K, 101.3 kPa and 10% O<sub>2</sub>)**

	Baseline	Test burn	ELV Vietnam
∑PAH (µg/m <sup>3</sup> )	1.8	0.49	–
HCB (ng/m <sup>3</sup> )	<31	<35	–
Benzene (mg/m <sup>3</sup> )	2.2	3.2	80
VOC (mg/m <sup>3</sup> )	17	26	200

**Table 3 – Gaseous compounds (mg/N m<sup>3</sup>)**

	Baseline	Test burn	ELV Vietnam
HCl	2.1	2.4	90
HF	<0.21	<0.23	4.5
NH <sub>3</sub>	<1.0	<0.44	45
CO	99	131	225
O <sub>2</sub> (%)	5.24	5.21	–
SO <sub>2</sub>	1.8	2.0	225
NO <sub>2</sub>	21	40	–
NO	760	1220	–
<b>NO<sub>x</sub> expressed as NO<sub>2</sub></b>	<b>1180</b>	<b>1910</b>	<b>1000</b>

below the emission limit value. Sampling and analysis were performed in accordance with US EPA Method 26A (Federal Register, 2000). Even if the insecticide contained both chlorine and fluorine, the emissions were not affected (Table 3).

The result for CO was well below the current emission limit value of 225 mg/N m<sup>3</sup> and independent of the insecticide disposal. 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 will be exhausted with the kiln gases. Control of CO is critical in cement kilns when ESP is 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. 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).

The result of SO<sub>2</sub> was less than 1% of the emission limit value (225 mg/N m<sup>3</sup>) and independent of the insecticide disposal. Ninety-nine percentages of the sulphur oxides emitted from cement kilns is in the form of SO<sub>2</sub> and originates mainly from sulphides and organically bound sulphur in fuels and raw materials (Oss and Padovani, 2003).

The reason for the high NO<sub>x</sub> levels during the test burn was due to high heat input through the main flame due to wrong information about heat content of the insecticide mix prior to the test. The coal feed was approximately 1 tonne higher than required. The easy burnability of the solvent of the insecticide mix compared to hard coal probably caused a more intense flame in the main burner as well as added 31 kg of nitrogen per hour. The consequence of this inadequate compensation was higher temperature in the kiln and higher NO<sub>x</sub> levels. The NO<sub>x</sub> level was however higher than the ELV also under the baseline measurements (under investigation). The result confirms what most studies have concluded with earlier, that more than 90% of the NO<sub>x</sub> emissions from cement kilns are NO, the rest is NO<sub>2</sub> (Oss and Padovani, 2003).

NO and NO<sub>2</sub> concentrations were monitored in accordance with US EPA Method 7E and sulphur dioxide concentrations in accordance with US EPA Method 6C (Federal Register, 2000).

#### 4.5.4. Results of solid particles and metals

The concentration of dust was 33 and 20 mg/N m<sup>3</sup> for the baseline test and the test burn, respectively, i.e. independent of the insecticide destruction. The ELV in Vietnam is

**Table 4 – Metal concentration in  $\mu\text{g}/\text{N m}^3$** 

	Baseline	Test burn	ELV
As	<5.4	<2.7	4500
Cd	0.71	0.74	450
Co	<0.54	<0.27	
Cr	1.7	4.3	
Cu	<1.1	0.71	9000
Hg	4.7	0.33	
Mn	12	14	
Ni	1.6	1.8	
Pb	<4.3	<2.2	4500
Sb	<3.3	<1.6	11250
Sn	71	38	
Tl	<2.7	<1.4	
V	<0.65	0.82	
Zn	13	2.7	13500

100  $\text{mg}/\text{N m}^3$ . Sampling of solid particles was conducted in accordance with US EPA Method 5 (Federal Register, 2000).

The analysis results of arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, antimony, tin, thallium, vanadium and zinc are given in Table 4. Vietnamese ELVs are given for arsenic, cadmium, copper, lead, antimony and zinc and all the results were 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 the insecticide destruction. The results of tin are probably due to contamination or interferences in the analytical technique used in the laboratory. Sampling and analysis of metals were 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).

#### 4.5.5. Solid samples and product quality

Raw meal, fine coal, ESP dusts and clinker were sampled every second hour during the 2 days and analysed for main and trace inorganic components as well as insecticides. The results showed no effect of the insecticide disposal. The clinker had an average concentration of chlorine of 18 and 19  $\text{mg}/\text{kg}$  under baseline and test burn conditions, respectively; the fluorine was <0.40  $\text{mg}/\text{kg}$  for all samples. All the dusts produced by the ESP are recovered and reintroduced back to the process, i.e. no residues or waste is produced.

Ordinary quality testing was performed on clinker, cement and concrete produced the 2 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, 3, 7 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

Already in the 1970s the pesticide industry knew by practise that even persistent compounds were completely destroyed at combustion temperatures around 1000 °C and a few seconds

retention time (Karstensen, 2006a). Laboratory studies and thermodynamic calculations confirm this. A cement kiln possess many inherent features which makes it ideal for hazardous chemicals treatment; high temperatures up to 2000 °C in the main flame, several seconds residence time, surplus oxygen, good turbulence and mixing conditions.

Some of the early projects carried out by GTZ and US Aid might have assumed that any cement kiln would qualify to destroy obsolete pesticides. Even though all cement kilns need high temperature to produce clinker, not all are necessarily suited for hazardous waste destruction without upgrading or modification. The feasibility has to be assessed case by case, and will depend on technical, chemical and environmental conditions, waste and raw material composition, location, infrastructure, policy and regulation, permit conditions, competence, acceptability etc. (Karstensen, 1998a,b; Karstensen, 2001a,b).

A feasible cement kiln will together with environmentally sound management and operational procedures, adequate safety arrangements and input control secure the same level of environmental protection in developing countries as in the EU and the US. As clearly illustrated in this study—instead of representing a threat to environment and health and causing problems for the owner, the hazardous insecticide was safely destroyed in a local cement kiln at same time as non-renewable fossil fuel was saved. The cost savings of using a local cement kiln will be considerable compared with other treatment options, also export, and can contribute to make developing countries self-reliant with regards to hazardous waste treatment. Building of hazardous waste incinerators imply large investments and high running costs and is normally not affordable to developing countries.

The test burn demonstrated the best destruction efficiency ever demonstrated; 10,000 times better than required by the US regulation, the most stringent in the world today. Except for the  $\text{NO}_x$  emissions, all the test results were in compliance with the Vietnamese regulation. The results of the PCDD/F measurements are in line with the results of a study on POPs emission from cement kilns conducted by the World Business Council for Sustainable Development (Karstensen, 2004, 2006b)—a study evaluating around 2200 PCDD/F measurements and concluding that co-processing of hazardous waste does not seem to influence or change the emissions of POPs from modern BAT cement kilns.

## 6. Conclusion

Continued accumulation and inadequate management of obsolete pesticides and POPs constitute a threat to health and environment, especially in developing countries. High-temperature combustion has shown to be the best way to destroy most of these chemicals but only a few projects utilising high temperature cement kilns have been reported and none has prior to this test been able to verify the destruction efficiency under developing country conditions.

The test burn conducted with two hazardous insecticides in a cement kiln in Vietnam demonstrated the best destruction efficiency ever measured. All the test results, except for the  $\text{NO}_x$ , were in compliance with the most stringent

regulations. This was the first time PCDD/Fs, PCBs and HCB were measured in an industrial facility in Vietnam and all the results were below the detection limits. This proved that the destruction had been complete and irreversible, and in full compliance with the requirements of the Stockholm Convention of being environmentally sound, i.e. not causing any new formation of PCDD/Fs, HCB or PCBs.

Environmentally sound disposal of hazardous chemicals is costly if export or new disposal facilities are considered and may not be affordable to many developing countries. Cement kilns are however commonly available in most countries and modern best available techniques kilns are nowadays primarily built in emerging markets. A feasible cement kiln can constitute an affordable, environmentally sound and sustainable treatment option for many hazardous chemicals if adequate procedures are implemented.

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