The Potential of using Cement Kilns for Environmentally Sound Destruction of Obsolete Pesticides in Developing Countries

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Abstract

The accumulation and bad 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 tons of obsolete pesticides are accumulated globally, especially in developing countries. Many of the accumulated obsolete pesticides are persistent organic pollutants POP's 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.

Several international environmental conventions aim to protect human health and the environment through measures which will destroy and irreversible transform stockpiled hazardous chemicals and reduce and/or eliminate emissions and discharges. These conventions acknowledge that there is an urgent need for environmentally sound destruction of hazardous chemicals and that developing

countries need to strengthen their national capabilities for safe management and disposal.

The Food and Agriculture Organization of the United Nations has been addressing this issue and disposed of approximately 3,000 tons of obsolete pesticides in more than 10 countries in Africa and the Near East since the beginning of the 1990's. The hazardous wastes has mainly been shipped to Europe for high-temperature incineration in dedicated facilities, a practise which does not stimulate development of local solutions and capacity building; it is also reasonable to anticipate that this approach involves higher costs and increased risks for accidents and spill.

The pesticide manufacturing industry started already in the 1970's to look into possible treatment options for obsolete pesticides and pesticide wastes and combustion was soon considered to be the best method. However, high temperature incineration is usually not available as a treatment option in developing countries. High temperature cement kilns however, are commonly available in most countries and has shown to constitute an affordable, environmentally sound and sustainable treatment option for many hazardous wastes if adequate procedures are implemented.

Cement kilns has been used for destruction of obsolete pesticides in developing countries on several occasions but so far not being able to verify the destruction performance in an unambiguous way. Such verification is established in a test burn, which is the only way to prove that the cement kiln is suitable for the purpose. The projects failed mainly due to improper technical preparation.

The lessons learned from these experiences were used to carry out a test burn with two toxic and obsolete insecticides in Vietnam in 2003. The destruction and removal efficiency was measured to be better than 99.999985% and demonstrated that

co-processing of hazardous chemicals can be done in an irreversible and environmental sound manner in a local cement kiln under developing country conditions. 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 showed 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.

Keywords: Obsolete Pesticides; POP's; Environmentally Sound Destruction; Developing Countries; Cement Kilns.

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1. Introduction

The accumulation and bad management of obsolete pesticides and other hazardous chemicals constitutes a threat to health and environment, locally, regionally and globally. Estimates indicate that more than 500,000 tons of obsolete pesticides are accumulated globally, especially in developing countries (FAO, 2001a). The Food and Agriculture Organization (FAO) of the United Nations has been addressing this issue and disposed of approximately 3,000 tons in more than 10 countries in Africa and the Near East since the beginning of the 1990's (FAO, 2001b). This means less than 1% of the accumulated amounts in a period of more than 10 years; if we anticipate a slower but continued accumulation in the years to come and approximately the same speed of disposal, this problem will “never” be solved. In addition to the clean up of obsolete pesticides, the world will also need funds and facilities for environmentally sound destruction of the persistent organic pollutants POP’s covered by the Aarhus Protocol (UNECE, 1998) and the newly ratified Stockholm Convention on POP's (UNEP, 2001).

Despite the fact that FAO (1999) has recommended that local destruction solutions for obsolete pesticide stocks should be supported as and when appropriate, pesticide waste from Africa has so far mainly been shipped to Europe for high-temperature incineration in dedicated facilities at an average cost of $3,500 per ton (Science in Africa, 2002). This practise involves high costs, considerable environmental risks due to long transport distances and doesn’t provide the necessary capacity building on hazardous waste management in the affected developing countries.

A considerable amount of the accumulated obsolete pesticides are persistent organic pollutants 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 (Jones and de Voogt, 1999; Vallack et al., 1998). 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 mixed stockpiled waste still represent locally and regionally important on-going primary source inputs of hazardous compounds to the global environment (Brevik et al., 2004).

Several international environmental conventions aim to protect human health and the environment through measures which will destroy and irreversible transform stockpiled hazardous chemicals and reduce and/or eliminate emissions and discharges of pesticides and persistent organic pollutants. Of special relevance is the Aarhus Protocol, the Stockholm Convention which entered into force 17 May 2004 and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes (Basel Convention, 1989) which aims to stimulate local treatment of hazardous wastes.

The Aarhus Protocol on Persistent Organic Pollutants covers 16 POP's, 11 of which are pesticides, which are Aldrin, Dieldrin, Endrin, Chlordane, DDT, Heptachlor, Hexachlorobenzene, Mirex, Chlordecone, Lindane, and Toxaphene. The Stockholm Convention on Persistent Organic Pollutants covers for the time being 12 POP's, which are Polychlorinated Biphenyls (PCB), Poly-chlorinated dibenzo-p-dioxins and dibenzo-furans (PCDD/Fs) and 9 of the same pesticides as the Aarhus Protocol, except Chlordecone and Lindane. Using the precautionary approach, the Stockholm Convention also enables the listing of new targets as threats are recognized. There is currently no reliable information available of what quantities these chemicals constitute on a global level, but it is reasonable to anticipate far more than the 500,000 tons accumulated obsolete pesticides.

These conventions acknowledge that there is an urgent need for environmentally sound disposal of the hazardous chemicals and that developing countries and countries with economies in transition, in particular the least developed among them, need to strengthen their national capabilities on sound management of chemicals (UNEP, 2001).

The preferred disposal option for these hazardous chemicals, high temperature incineration, is usually absent as a dedicated technology option in developing countries. However, high temperature cement kilns are common and available in most developing countries and can constitute an affordable, environmentally sound and sustainable treatment alternative.

Huge resources have been spent in recent years to investigate emerging and hopefully non-controversial and non-polluting technologies (UNEP, 2004). Unfortunately, many of the “emerging” technologies have low capacities (some are still in laboratory scale), are technically sophisticated and currently not affordable by many developing countries. A thorough and objective comparison with the state of the art technology on aspects like sustainability, suitability, performance, robustness, cost-efficiency, patent restrictions (availability), competence requirements and capacities is today urgently requested by nations struggling to get rid of these hazardous chemicals.

POP’s have been shown to interfere with hormone function and genetic regulation and in animal studies, myriad dysfunctions can be induced (manifested later in life) by low-dose POP’s exposure during development. The ubiquity of POP’s in biological tissue makes all organisms subject to developmental exposure (WHO, 2003; Godduhn and Duffy, 2003; Jobling et al., 2004; Gupta, 2004; McDonal, 2002; DeVito and Birnbaum, 1995). The Arctic, where subsistence living is common, is a sink region for POP’s and the arctic peoples now insist in action. Norwegian and Canadian researchers find more POP's and PCB's 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 POP's concentration in fish and other animals in the Barents sea the last 10-15 years (Gabrielsen et al., 2004).

To be able to implement the objectives of the conventions there will be a huge need for capacity building and cost efficient and environmentally sound destruction options primarily in developing countries. In Norway, cement kilns have been the only treatment option for organic hazardous wastes since 1980 and this has shown to be an environmentally sound and cost-efficient solution (Viken and Waage, 1983; Benestad, 1989). This paper provides an overview of thermal destruction in general and the possibilities of using local cement kilns in particular.

2. Thermal destruction

Combustion is a combination of pyrolysis and oxidation. Pyrolysis is a chemical change resulting from heat alone and involves the breaking of stable chemical bonds, often resulting in molecular rearrangement. Oxidation is the gross reaction of an organic species with oxygen and requires relatively low activation energies (Niessen, 1995). For efficient combustion, oxidation should be the dominant process, with pyrolysis occurring either incidentally to the oxidation or to put a material into a better physical form for oxidation. To combust hazardous wastes effectively, pyrolysis must be efficient and complete before oxidation of the molecular chemical by-products can occur.

To achieve a complete thermal destruction, sufficient temperature, oxygen supply, residence time and mixing conditions are needed (Brunner 1993; Dempsey and Oppelt, 1993). Both dedicated hazardous waste incinerators and cement kilns can achieve a complete thermal destruction of mixed hazardous wastes, but normally cement kilns have higher temperature and longer residence times than incinerators (Freeman, 1997). This is why cement kilns are ideal; flame and kiln gas temperatures up to 2,000°C and long residence times up to 8 seconds ensures complete pyrolysis and surplus oxygen ensures complete oxidation (Freeman, 1997).

Combustion temperature and residence time needed for mixed hazardous wastes cannot be readily calculated and are often determined empirically. Some common solvents such as alcohols and toluene can easily be combusted at lower temperatures, while other more complex organic halogens require more stringent conditions such as the United States Environmental Protection Agency (US EPA) Toxic Substances Control Act (TSCA) PCB incineration criteria of 2 seconds residence time at 1,200°C and 3% excess oxygen in the stack gas (Federal Register, 1999) or the European Council Directive 2000/76/EC on the Incineration of Waste criteria of 1100°C for at least two seconds if more than 1 % of halogenated organic substances are incinerated (Council Directive, 2000).

Combustion and other forms of thermal treatment have, over the years, been adopted as proven technologies to dispose of hazardous waste, municipal solid waste, and medical waste regulated under the Resource Conservation and Recovery Act RCRA and toxic substances under the Toxic Substances Control Act TSCA (Lee et al., 2000; Dempsey and Oppelt, 1993). Pesticides constitute a considerable part of the compounds regulated under the TSCA (Ferguson and Wilkinson, 1984).

2.1 Thermal destruction of pesticide wastes, POP's and other hazardous chemicals

Pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pests are living organisms that occurs where they are not wanted or that cause damage to crops or humans or animals.

Though often misunderstood to refer only to insecticides, the term pesticide also applies to herbicides, fungicides, and various other substances used to control pests (Pesticide Manual, 1997).

The pesticide manufacturing industry started early to look into possible management and treatment options for obsolete pesticides and pesticide wastes and in the 1970's and 1980's a number of research and demonstration studies were conducted to identify the best disposal options for pesticides and pesticide wastes. Combustion was soon considered to be the best method and several key research projects confirmed this in pilot and commercial available incinerators (Ferguson and Wilkinson, 1984).

In a study comparing chemical and thermal methods for disposal of 20 pesticide chemicals Kennedy et al. (1969) concluded that incineration is superior to chemical methods for the destruction of pesticides and that most pesticide compounds are destroyed effectively by burning at temperatures 800^{o}C to 1000^{o}C (Atkins, 1972).

In 1977 the US Air Force incinerated 8.7 million liters of Agent Orange and the destruction efficiency was estimated to be at least 99.99% (Ackerman et al., 1978).

General Electric incinerated 6,000 liters of 20% liquid DDT formulations with temperatures ranging from 870^{o}C to 980^{o}C and retention time of up to 4 seconds achieving destruction efficiency better than 99.99% (Leighton and Feldman, 1975).

DDT and 2,4,5-T formulations constituting 20% of the solid input were destroyed in a municipal sewage sludge incinerator with an average temperature ranging from 600^{o}C to 690^{o}C and destruction efficiencies from 99.95% to 99.99% (Whitmore, 1975).

The University of Dayton achieved destruction efficiencies exceeding 99.99% at 2 seconds retention time for DDT, DDE, Diazinon, Endrin, Hexachlorobenzene, Kepone, Mirex and Pentachloronitrobenzene in an incinerator operating at 900^{o}C (Duvall and Rubey, 1976).

The Midwest Research Institute carried out pilot studies on thermal decomposition of Aldrin, Atrazine, Captan, DDT, Malathion, Mirex, Picloram, Toxaphene and Zineb in 15 liquid and solid formulations and the destruction efficiencies generally exceeded 99.99% over a range of temperatures and retention times; 950^{o}C to 1100^{o}C, 1.2 and 6 seconds (Ferguson et al., 1975).

In a study for the US Army, TRW Systems investigated the thermal destruction efficiencies of Chlordane, 2,4-D, DDT, Dieldrin, Lindane and 2,4,5-T at a temperature of 1000^{o}C and 0.4 second retention time. The destruction efficiencies exceeded 99.99% (Shih et al., 1975).

The Los Alamos National Laboratory investigated for US EPA the thermal destruction efficiencies of Pentachlorophenol at a temperature of 980^{o}C and 2.5 second retention time. The destruction efficiencies exceeded 99.99% (Stretz and Vavruska., 1983).

In a review of incineration options for pesticide wastes, Oberacker (1988) lists ranges of pesticide formulations of DDT, Aldrin, Picloram, Malathion, Toxaphene, Atrazine, Captan, Zineb, Mirex, Herbicide orange (including dioxins and furans), PCP, Kepone and Chlordane and their thermal destruction efficiencies in different incineration tests. The exceptions to the rule of achieving destruction efficiencies better than 99.99% was when the pesticide concentration was very low (created problems with the analytical detection limits), when solids were not properly mixed, when products of incomplete combustion (PIC's) appeared or in cases were the temperature were deliberately reduced to determine the operational bounds of effective performance. Potential problems with certain heavy metals and compounds like bromine and iodine were questioned in the review. Some metals were included in the incinerator tests, including lead, zinc, arsenic, chromium and others, without creating any problems.

In 1989 Oberacker investigated the incinerability of Ethylene di-bromide (EDB), Dinoseb and 2,4,5-T. The EDB molecule contains approximately 85% bromine by weight and earlier studies had resulted in visible bromine gas emissions from the incinerator stack when EDB was incinerated. This problem was solved completely in the US EPA test burn by adding 10% dilute sulphuric acid. Approximately 75,000 liters of an EDB/ ethylene dichloride and carbon tetra chloride mixture and 20,000 liters of an EDB/ chloropicrin formulation were incinerated and all compounds achieved destruction efficiencies better than 99.9999%. No bromine was detected in the stack, detection limit of 4-5 $\mu g/m^3$. Two Dinoseb formulations were incinerated at a feeding rate of up to 180 liters per hour, achieving destruction efficiencies better than 99.999%. The test results for 2,4,5-T was not ready when the article was written but EPA was confident that incineration was feasible.

In a study by Oberacker et al. (1992) the air emissions and residues from open burning of used pesticide bags contaminated with Thimet and Atrazine in farm field conditions were characterised. While the amounts of particulates were high, the toxic releases appeared small in terms of posing any significant health or environmental risk.

The US EPA also carried out a number of studies on industrial organic hazardous wastes in different incinerators and the following compounds were found to be incinerable to the 99.99% or better destruction level: PCB's, Toluene, Tetrachloroethylene, Trichloro-ethylene, Carbon tetrachloride, Naphtalene, Chloroform, Methylene chloride, Methyl ethyl chloride, Phenol, Benzene, Butyl benzyl phthalate, Chlorobenzene, 1,1,1-Trichloro-ethane, Aniline, Benzyl chloride, Diethyl-phthalate, Phthalic anhydride, Amines, Chlordane, Chlorobenzenes, Chloromethane, Chlororethanes, Cresols, Dimethyl phenol, Dodecanol, Hexachlorobutadiene, Isocyanates, Methylene bromide, Methyl pyridine and Phosgene gas (Oberacker, 1988).

The incinerability of pesticides and hazardous wastes were also investigated in different high temperature production processes, like brick kilns, cement kilns, oil furnace process, blast furnace, lime kilns, glass kilns etc. The conclusion of the study showed a limited potential for the use of most of these facilities for pesticide treatment, with the exception of cement kilns (Hall et al., 1983).

2.1.1 Cement production and co-processing of hazardous wastes

In short, cement is made by heating a mixture of calcareous and argillaceous materials, usually in huge rotary kilns, to a temperature of about 1450°C. In this process, partial fusion occurs and nodules of so-called cement 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. In the clinker burning process it is essential to maintain a kiln charge temperature of approximately 1450°C. Also, the clinker needs to be burned under oxidising conditions (Integrated Pollution Prevention and Control, 2001; Duda, 1985).

Fuel and wastes fed through the main burner will be decomposed under oxidising conditions in the primary flame burning zone at temperatures up to 2,000°C and a retention time up to 8 seconds. Fuel and waste fed to the secondary burner, preheater or precalciner will be burnt at temperatures between 800°C and 1,200°C. Cement kilns are equipped with either electro static precipitator (ESP’s) or fabric filters, or both, for particulate matter control. Acid gas pollution control devices are not used at cement kilns (except for SO_2 in some instances) since the raw materials are highly alkaline and provide acid gas control.

3. Destruction of obsolete pesticides and POP’s in developing countries using cement kilns

Several pilot projects have been using cement kilns for disposal of obsolete pesticides and POP's in developing countries the last 20 years.

3.1.1 Malaysia

The German Deutsche Gesellschaft fuer Technische Zusammenarbeit (GTZ) carried out the first reported disposal operation with obsolete pesticides using a cement kiln in Malaysia in the middle of the eighties (Schimpf, 1990). The cement plant had a dry rotary kiln with a diameter of 4.3 meter and a length of 73 meter. The plant was equipped with electrostatic precipitator and produced 3,800 tons of clinker per day.

Solid and concentrated liquid pesticides were dissolved in kerosene and fuel oil in a 5 m^3 storage tank with an agitator and feeded 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 combustion, dust samples were taken from the ESP and analysed for PCDD/F. No PCDD/F's where found (Schimpf 1990).

Unfortunately, the report provides no information about the amounts of pesticides destroyed, the concentration of the active ingredients, the feed rate into the kiln or the destruction and removal efficiency. The cost for the plant modification, i.e. the introduction system, was estimated to be 12,000 USD (Schimpf 1990).

3.1.2 Pakistan

A total of 17,000 litre of 9 different organophosphates and 3 different organochlorines pesticides mixtures were destroyed in a cement kiln in Pakistan by the US Aid in 1987 (Huden, 1990).

The cement plant was a modern, 4-cyclone, preheater dry process plant built in 1986 with a clinker production of 2,000 tons per day. The plant used fuel oil with an approximate heating value of 45 MJ/kg and a sulphur content of 2.9 percent. Fuel oil was fed to the kiln through a Pillard burner at a rate of 7.3 tons per hour. The inside diameter of the kiln was 4.3 meter and the length 78 meter. Air from the raw material crushing and blending operation was combined with the kiln gases and exhausted to an electrostatic precipitator. The outlet of the electrostatic precipitator was connected to a 35 meter high stack. The average volumetric flow rate was measured to be approximately 204,000 Nm^3/hour.

Stack gases were sampled and analyzed to determine particulates, chlorides, oxides of sulphur and carbon monoxide emissions. The results met post-1990 standards of the Environment Protection Agency of Punjab. Products of incomplete combustion PIC's were examined via GC/MS, but no PIC's were detected. Analyses of process samples, raw meal feed, and clinker and ESP dust showed no detectable pesticides.

Feasibility decision of the test burn assumed that sufficient quantity (a minimum of 12,000 litres) of one organophosphate and one organochloride pesticide would be made available. For the purposes of the test burn it was essential to have a product of reasonable quality that had an active ingredient close to the original formulation but not less than 25% and of a viscosity close to that of water. Early sample analysis, however, indicated poor quality, with an active ingredient in the zero to 10% range and high viscosity. In order to work with a sufficient quantity the team realised that a ”cocktail” of various organophosphates and organochlorines was inevitable. This, of course, added innumerable unknowns and analytical and process challenges to the task.

All the collected pesticides had been sampled and analysed for active ingredient and other physical characteristics beforehand, and declared fit for use. They represented best available grades within a reasonable transport radius from the plant.

The pesticide delivery system was designed for free flowing liquids. Waste pesticides were pumped from a tank truck and injected at an average rate of 294 litres per hour for the organophosphates and 46 litres per hour for the organochlorines. The injector achieved fine atomisation using compressed air and was tested successfully with diesel fuel. The ”cocktail” of pesticides, however, contained sludges 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 RCRA standards for particulate concentrations (183 mg/m^3) but DRE requirements and HCl emissions limits were not met.

3.1.3 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 lb) in accordance with the WHO (2002) classification. The insecticide is highly toxic to fish and is explosive in its dry form.

The German GTZ initiated a clean up project in 1993 were DNOC firstly was transferred from rusty and leaking drums into new and chemical resistant containers and brought to a central storage place (Schimpf, 1998). The Ministry of Agriculture was the formal owner of the DNOC and was responsible for the administrative processing within Tanzania. It filed an official application for incineration of the DNOC in the cement plant to the Ministry of Environment in 1992. The incineration permit was issued by the National Environmental Management Council and the Chief Government Chemist four years later, in 1996.

A test burn with 1:1 DNOC/diesel-mixture was performed in the Twiga Portland Cement kiln west of Dar-Es-Salaam in 1996. The cement plant had three dry preheater kilns of different sizes, and kiln 3 was assumed to be suitable for incinerating the DNOC (Schimpf, 1998). Clinker and filter dust samples were taken before, during and after the test run. The samples were analysed at two laboratories for DNOC residues. A heated measuring probe sampled flue gas 70 metres up in the stack and measured CO, CO_2, O_2, NO_x and the temperature continuously. The composition of the flue gas and the temperatures fluctuated. During the test burn no DNOC residues were detected in the clinker or the filter dust (Schimpf 1998).

A waste introduction system was designed and consisted of a high-pressure pump resistant to chemicals, storage and mixing steel tank with a capacity of 4,4 m^3 with integrated filter system and all the necessary safety components. This waste introduction system was placed in a 20-foot container and installed in a steel drip tray so that any possible leaks of the contents of the tank could be caught in the tray. The DNOC was diluted with 50% diesel oil in the tank to a concentration of below 10% active ingredient and then fed automatically and continuously directly into the flame at high pressure via the fuel lance. The calorific value of the DNOC/diesel-mixture was measured to be 46 MJ/kg and the mixture was pumped at a rate of 320-350 litres per hour, with a diaphragm pump through the oil lance into the kiln. The fuel oil was fed at a rate of 3300-3500 litres per hour (Schimpf 1998).

Approximately 57,500 litres DNOC 20% were incinerated in kiln 3 within a period of about 7 weeks. The DNOC was diluted with the same quantity of diesel oil, thus, altogether, approximately 115,000 litres DNOC-diesel were introduced into the cement kiln and incinerated. The 400 old DNOC drums were melted and recycled as iron for construction purposes.

A series of technical problems led to delays, especially during the testing phase. The kiln "*broke down*" regularly during the incineration of the DNOC due to several problems. The refractory of the kiln was damaged, the outer wall of the satellite cooler burned through, the power fluctuated and went down now and then and the raw meal feed was disrupted (Schimpf 1998).

At the beginning, during the preparatory phase, the workers at the cement plan viewed the activities of the team very sceptically. Directly before the start of the test run there was a ”strike” by the workforce, they wanted to prevent the incineration. After discussions with the union leader, it turned out that the responsible liaison officer commissioned by the management had not carried out his tasks and the workers had not been informed correctly of the proposed measure. Their behaviour altered as soon as the representatives responsible for the project explained the project and the task of the waste introduction system to the workers in an information session. After this the negative attitude changed to support (Schimpf 1998).

The cost for the disposal was estimated to be approximately 4,300 US$ per ton of DNOC, a cost lying in the "*upper range of normal disposal costs*" according to Schimpf. However, the cost estimate included the entire project, i.e. 245,000 US$ over four years, covering collection and safeguarding measures, transport, field costs, new containers and personal protection equipment, construction of the waste introduction system with pumps, flow meters etc., diesel oil for dilution of the DNOC, cost for analysis, personnel and travel.

3.1.4 Poland

In a Polish test burn recently reported by Stobiecki et al. (2003) different mixes of 12 obsolete pesticides and POP's were introduced into a cement kiln (no details about the process type or operating conditions) over a period of three days.

The different pesticide mixtures were blended into three batches with light heating oil. Batch 1 constituted 10 tons with a total pesticide content of 11.5% and 2.3% active ingredients of the following pesticides: Methoxychlor, γ-HCH, α-HCH, Fenitrotion, Fention, DDT, Endosulfan and Dichlorobenzene. Batch 2 constituted a total pesticide content of 29.4% and 6% active ingredients of the following pesticides:

Methoxychlor, DNOC, DDT, Endosulfan, γ-HCH, α-HCH, Dichlorobenzene and Esfenwalerat. Batch 3 constituted a total pesticide content of 30.5% and 6.4% active ingredients of the following pesticides: Metoxychlor, Fenitrotion, DNOC, γ-HCH, α-HCH, DDT, Carbosulfan, Deltametrine, Endosulfan, Dichlorobenzene and Esfenwalerat. The heating value of the three batches was 44,545, 43,193 and 42,968 kJ/kg respectively.

The mixes were fed through the main burner 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 0.02 and 1 $\mu g/m^3$) or in the clinker (detection limit between 0.001 and 0.05 mg/kg). Physical and chemical testing of clinker gave normal and similar results for all conditions. The PCDD/F emissions was 0.009 ng I-TEQ/Nm^3 with coal only and 0.015, 0.053 and 0.068 ng I-TEQ/Nm^3 when feeding the three alternative fuel mixes with pesticides respectively.

3.2 Planned but not completed disposal operations

Some projects have planned or investigated the possibility of using a local cement kiln for obsolete pesticide destruction in developing countries but have been forced to halt due to public perception, opposition or technical constraints.

In 1997 the Danish Government decided to support a project involving the collection and treatment of obsolete pesticides spread around in Mozambique. The over all intention of the project was to clean up the country by disposing the obsolete pesticides in a local cement kiln and to transfer capacity and to leave behind a permanent facility for future sound organic hazardous waste disposal (Jannerup, 1998). Almost 1,000 tons of pesticides where collected throughout the country and stored intermediately in special transport containers. A central waste receiving, storage and treatment station was built close to the cement plant Cimentos de Mozambique in Matola. The intention was to upgrade the cement kiln and to destroy those organic obsolete pesticides which fulfilled the incineration criteria. Materials containing heavy metals or unidentified material were out of scope. However, NGOs in South Africa and the community of Matola started to oppose and question the intentions of the project. The media mentioned the project badly, it became controversial and it was decided to put the disposal into a standstill. When Mozambique was hit by a flood in February 2000 the waste station in Matola was affected and the authorities wanted to commence with the disposal. A review team assessed the situation and it became soon evident that the project preparation had not been satisfactory and that the cement kiln were not feasible to dispose of highly chlorinated pesticides due to various reasons (Karstensen, 2000). Cimentos de Mozambique had also received bad mention in the media and feared for their market shares. Finally in July 2000, the cement kiln upgrading was stopped and the pesticides exported to Europe.

In the period from 1989 until 1993 114 tons of obsolete pesticides were disposed of secretly in Nepal by spreading over land or pouring into rivers. A plan to dispose of the pesticides in the Hetauda and Jaljale cement factory in 1998 was halted due to negative perceptions, lack of technical understanding and high cost estimates. Still 74 tons of expired pesticides are waiting for disposal in warehouses in Kathmandu, Nepalganj and Amlekhganj, whereof 36 tons are persistent organic pesticides (Nepali Times, 2004).

The feasibility of using a local cement kiln for obsolete pesticide destruction was investigated in a NATO clean up project in Moldova (Karstensen, 2004b). An inventory of obsolete pesticides and POP's had been performed under the enabling activities related to the implementation of the Stockholm Convention in Moldova and showed that approximately 1,700 tons of more that 150 different formulations are stored in nearly 360 locations around the country (POP's Inventory, 2003). The cement plant, a dry production process with a four stage suspension preheater, located north of Rezina town and west of the river Dnestr was evaluated. The NATO feasibility study however, recommended not to continuing with the cement kiln option due to cost and possible time constraints. Various technical changes were recommended, which under the current market situation would be difficult to defend financially by the cement company.

3.3 Lessons learned from the demonstration projects

The absence of PCDD/F's in the ESP dust in the first GTZ operation in Malaysia is ensuring but certainly not enough to verify the performance of a cement kiln. However, there is no reason to believe that the 2,4-D and 2,4,5-T were not safely destroyed in the main flame of the kiln but the DRE should have been established.

For the purpose of the pilot and demonstration burn in Pakistan it might had been wise to insist on using a uniform, higher grade waste pesticide and restricting the burn to one compound in each pesticide group, as had been intended. 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. 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 burn. The choice of laboratory is of course also important. Huden (1990) speculated that the concentration of pesticides in the feed was too low for instrumentation to measure a DRE of 99.99%, probably due to a combination of low active ingredient and low feed rate. Had it been possible to feed a higher concentration to the kiln, the desired DRE could have been demonstrated instrumentally. Further on, in selecting a cement plant for waste disposal, 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 team was affected by management changes in some of the ministries; the acceptance and easy approval process at the feasibility stage did not automatically guarantee approval from the new generation of bureaucrats. Agreements in principle should have been formalised early so that promises once made represented institutional instead of individual commitment. According to Huden, the important public relations issue was given short shrift. 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.

Obviously, the kiln chosen for the disposal operation of DNOC in Tanzania (Schimpf 1990) was not the best choice. 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 determine the destruction and removal efficiency of DNOC in the kiln. To measure DNOC in ESP dust and clinker is not sufficient; the exit gas is the most important. The measurement of CO_2, O_2 and NO_x in the exit gas does not give any information about the DRE. The project clearly showed the necessity of transparency, information and good communication with all involved parties.

The planned upgrading and disposal in the cement kiln in Mozambique failed due to proper preparation and lack of public information and awareness raising. Competence, good communication and transparency are certainly the key.

Obviously, some of the described projects may have assumed that any cement kiln would be suited for the purpose. Even though all cement kilns needs high temperature to produce cement, not all are necessarily suited without upgrading or modifications. 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, acceptability etc. (Karstensen, 1998 a and b; Karstensen 2001 a and b).

4. Test burn with obsolete pesticides in Vietnam

Approximately 10,000 tons of dioxin-contaminated soil stemming from herbicide spillage during the Vietnam War and more than 225 tons of 200 different obsolete pesticides and 1.7 million containers are currently accumulated in more than 100 locations in Vietnam (Karstensen et al., 2003b).

The only option for treatment of hazardous wastes in Vietnam is currently smaller static incinerators or the mobile incinerator of Ministry of Defence (Karstensen et al., 2003a). Both options imply discontinuous incineration with low capacity and at lower temperatures. As many of these devices would not comply with international recognised performance standards we wanted to investigate if a local cement kiln could be used. A joint project with representatives of the authorities and the cement plant owner was initiated were the objective was to carry of 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 clinker production is performed in a dry suspension preheater cement kiln equipped with a precalciner. The kiln 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 cement clinker per day. The kiln is fired with coal through two burner systems, the main burner and the precalciner, 7 tons and 13 tons per hour respectively. The normal fuel is anthracite coal with an average calorific value of 30 mega joule/kg.

A solvent-based insecticide with two active ingredients, 18.8% Fenobucarb and 2.4% Fipronil, was identified to be a suitable test burn candidate as it contained aromatic molecules with chlorine and fluorine.

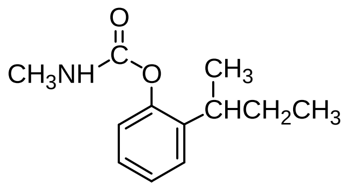

Fig. 1 Chemical structure of Fenobucarb.

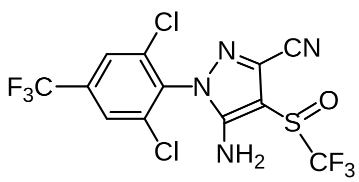

Fig. 2 Chemical structure of Fipronil.

The insecticide had expired and approximately 40,000 litres was stored in Dong Nai Province North of Ho Chi Minh City in 200 steel drums waiting for a sound disposal solution. The heat content of the insecticide was approximately 30% higher than the coal used by the cement plant. A steel storage and feeding tank for the insecticide was built at the plant and the tank was connected to the light fuel oil pumping system with automatic dosage and switch off/on through the main control system. The insecticide was pumped into the main flame together with coal through a three channel burner. The test burn was conducted over two days, 16 and 17 October 2003, starting the first day with a baseline study, i.e. feeding coal only. The second day, insecticide was introduced through the main burner at a rate of approximately 2,000 liters per hour, substituting approximately 2.5 tons of coal per hour. All together 39,500 litre was destroyed in the kiln in less than 20 hours.

The analysis results of stack gas sampling for the two days were compared with the Vietnamese emission limit values (ELV). The insecticide components fed to the kiln, Fenobucarb and Fipronil were not detected in the exit gas or any other sample collected during the test. The destruction and removal efficiency of Fenobucarb was better than 99.999997% and better than 99.999985% for Fipronil. There is no requirement to demonstrate the destruction and removal efficiency in a test burn in Vietnam, but compared to the most stringent requirement in any regulation today, US cement kiln operators would need to demonstrate a DRE of 99.99% for these 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. All these compounds, and many others, were analysed but all the results were below the detection limit, showing that the destruction had been complete and irreversible, i.e. no new formation of dioxins, furans or PCB's.

Raw meal, clinker, fine coal, electro static precipitator dusts were sampled every second hour during the two days and analysed, showing no effect of insecticide co-processing. Ordinary quality testing was performed on clinker, cement and concrete produced the two days and the results was within normal ranges and showed that the product quality was unaffected by the introduction of the insecticide.

5. Discussion

Less than 1% of the estimated accumulated amounts of obsolete pesticides spread around the globe have been disposed of since the beginning of the 1990's and proves the inability of the strategy chosen to solve the problems. To ship hazardous chemicals long distances to Europe for high temperature incineration in dedicated facilities is not optimal and shows lack of confidence in developing countries. The bad management of hazardous chemicals constitutes a serious threat for health and environment and needs to be dealt with in a cost-efficient and responsible way.

Cement kilns are being used for environmentally sound management of hazardous wastes and chemicals in many countries and testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of combusting wastes in cement kilns was first considered.

Numerous tests around the world 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 (Ahling, 1979; Benestad, 1989; Chadbourne, 1997; Karstensen, 1994; Lauber, 1982 and 1987). Comprehensive emission studies have also been performed when hazardous waste was introduced, and these have generally concluded that no significant differences could be measured between usages of the two fuels (Mac Donald et al., 1977; Suderman and Nisbet, 1992). For example, Branscome et al (1985) observed that "no statistically significant increase in emission rates were observed when the waste fuel (as opposed to coal) was burned".

Studies on dioxin emissions have also come to this conclusion (Abad et al., 2004; Branscome et al, 1985; Lauber, 1987; Garg, 1990; Schumacher et al., 2002). In general, the level of dioxins emitted during the use of conventional fuel was similar to their concentration when hazardous waste was introduced into the kiln. In a study performed for the World Business Council for Sustainable Development data from more than 1,700 PCDD/F measurements from wet and dry kilns, performed under normal and worst case operating conditions, and with the co-processing of a wide range of hazardous wastes fed to both the main burner and to the precalciner shows that most cement kilns can meet an emission limit of 0.1 ng TEQ/Nm^3 (Karstensen, 2004a).

Some of the pilot projects done in developing countries for treatment of obsolete pesticides using cement kilns might have assumed that any kiln would qualify. However, not all kilns are suited without upgrading or modifications and the feasibility should be assessed in case by case. Had only parts of the money spent by the global society looking for emerging technologies been used to establish sound practises for destruction of hazardous chemicals in cement kilns, many developing countries would have been self reliant with regards to hazardous waste treatment today. The test burn in Vietnam demonstrated that the introduced insecticides and all the POP's, i.e. dioxins, furans, PCB's and Hexachlorobenzene were below the detection limit and that the destruction had been complete and irreversible.

Conclusion

The Food and Agriculture Organization of the United Nations (FAO) has been addressing obsolete pesticides and successfully disposed of approximately 3,000 tons in more than 10 countries in Africa and the Near East since the beginning of the 1990's. The obsolete pesticide waste has so far mostly been shipped to Europe for high-temperature incineration in dedicated kilns. This practise involves high costs, considerable environmental risks due to transport and does not ensure adequate capacity building on hazardous waste management in the affected developing countries. Such a solution may solve the immediate risks of the obsolete pesticides but is not in agreement with the intention of the Basel Convention and does not leave any capacity behind.

So far, only a few disposal operations utilising cement kilns are reported. Only one, in Vietnam has been able to verify the destruction and removal efficiency DRE in a test burn, in fact the only way to prove the performance. The test burn clearly demonstrated the suitability of the cement kiln to co-process obsolete pesticides and that a controlled substitution of fossil fuel with hazardous waste is doesn't affect the emissions. The destruction and removal efficiency DRE was measured to be better than 99.999997% for Fenobucarb and better than 99.999985% for Fipronil. These results can be compared with the most stringent regulatory requirements in the world today, namely the USA, were cement kilns combusting hazardous wastes must perform a similar test burn and demonstrate 99.99% destruction and removal efficiency (DRE) for such 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 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.

Large amounts of hazardous wastes and chemicals constitute a serious threat to health and environment all over the globe and a well operated and suited cement kiln can constitute a sustainable and environmentally sound option for destruction of hazardous chemicals and wastes in many developing countries.

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