



4014 NW 13th STREET
 GAINESVILLE, FL 32609-1923
 352/377-5822 ▪ FAX/377-7158

KA 307-10-17
 April 13, 2011

RECEIVED
 APR 15 2011
 BUREAU OF
 AIR REGULATION

Mr. Jeff Koerner
 Bureau of Air Regulation
 Florida Dept. of Environmental Regulation
 2600 Blair Stone Road, MS 5500
 Tallahassee, Florida 32399-2400

**RE: Comments and Requests on Draft AC Permit 0530021-031-AC
 Short Term Trial Test of Specific Alternative Materials
 CEMEX Construction Materials Florida, LLC**

Dear Mr. Koerner:

The following comments provided for changes the draft AC permit, 0530021-031-AC. These changes are in addition to the comments sent to Christy Devore via email on April 7, 2011.

Page 1. Project Description:

The listing of fuels of on-specification used oil is requested to include off-specification oil. Similar to the Cemex Miami cement plant Title V permit language, we suggest the following language.

On-specification/Off-specification used oil burned at this facility shall not be a hazardous waste as defined by Rule 62-730.030, F.A.C., or 40 CFR Part 261. It shall not include fuels or blended fuels consisting in whole or in part of hazardous waste or which include mixture of any solid waste generated from the treatment, storage, or disposal of hazardous waste. Used oil shall be burned in compliance with Section 403.769(3), F.S.

iii. *On-specification/Off-specification used oil* samples shall be analyzed by EPA Recommended Analytical Procedures for Used Oil for the following constituent/property, associated unit, and using the test methods indicated in Table below:

Constituent/Property	Unit	Test Method
Cadmium	ppm	EPA SW-846 (6010)
Arsenic	ppm	EPA SW-846 (6010)
Chromium	ppm	EPA SW-846 (6010)
Lead	ppm	EPA SW-846 (6010)
Total Halogens	ppm	EPA SW-846 (9252)
Sulfur	percent	ASTM D129 or ASTM D1552
Flash Point	degree F	EPA SW-846 (6010)
Heat of Combustion	Btu/gal	ASTM D240
Polychlorinated Biphenyls (PCBs)	ppm	EPA SW-846 (6010) and EPA 680

NOTE: Other test methods may be used only after receiving written prior approval from FDEP.

Page 3. Proposed Project.

The listing of fuels of on-specification used oil is requested to include off-specification oil, as *On-specification/Off-specification used oil*.

The listing of fuels of on-specification used oil is requested to include off-specification

Page 6. Temporary equipment.

We request to include temporary grinding equipment. Revised PSD threshold calculations and Fugitive Emission, including grinding, calculations are included in the following table. The following additional language is suggested.

“An electric or diesel-powered shredder (approximately 630 horsepower); and other miscellaneous equipment to unload, store and handle the alternative fuels. Only diesel fuel shall be fired.”

Emissions Estimate of Alternative Fuel Grinding/Handling/Injecting
Created: April 12/2011
Cemex Construction Materials Florida, LLC, Brooksville cement plant

STEP	Action/Tasks	generic description	% of Total Throughput	PM Emission Factor ^h	PM ₁₀ Emission Factor ^h	PM Emissions tons	PM ₁₀ /PM _{2.5} Emissions tons	Emission Factors ^c	hours	SO ₂ Emissions tons	CO Emissions tons	NO _x +NMHC Emissions tons
		Receive materials by covered truck. Fugitive emissions: 1.4 miles per round trip x 59,400 tons/15 tons/trip (conservative estimated density) = 5,544 miles.										
1	Assume PM10 = PM.	transporting	100	0.524 lb/VMT		1.453	1.451					
2	Store under cover (to prevent stormwater runoff and fugitives).				<i>negligible when stored under cover (West Hall building)</i>							
3	Load material by front loader into optional grinder hopper. ^a	loading	100	8.74E-05 lb/ton	4.134E-05 lb/ton	0.00260	0.00123					
4	Grinder ^h	grinding engine	100	0.0012 lb/ton	0.00054 lb/ton	0.03564	0.01604					
	Grinder engine emissions							0.15 gr/bhp.hr				
	630 horse power engine operating for 1188 hours (59,400 tons @ 50 tons/hr)							0.929 gr/bhp.hr	1188	0.731		
								3.7 gr/bhp.hr	1188		2.911	
								3.0 gr/bhp.hr	1188			2.400
	Screen ^a	screening engine	100	0.00014 lb/ton	0.000046 lb/ton	0.00416	0.00137					
	Screen engine emissions					0.06358	0.02208	0.2 gr/bhp.hr				
	100 horse power engine operating for 1188 hours (59,400 tons @ 50 tons/hr)							0.929 gr/bhp.hr	1188	0.122		
								2.6 gr/bhp.hr	1188		0.341	
								3.0 gr/bhp.hr	1188			0.393
5	Half (1/2) inch or less material transported to precalciner staging area. 1000 ft/trip x 59,400 tons/15 tons/trip (estimated average density) x 1 mile/5280ft = 750 miles EF = 0.524 lb/VMT (see initial submittal)	transporting	100	0.524 lb/VMT		0.197	0.197					
6	Prepared material loaded by front loader into the pneumatic feed hopper. ^a	loading without cover	100	8.74E-05 lb/ton	4.134E-05 lb/ton	0.00260	0.00123					
7	Pneumatic biomass feeder system emissions	electric engine										
Total =						1.805	1.706			0.853	3.252	2.793

Based on process rates of: **total = 59,400 tons of alternative fuels**

Notes:

- ^a This screen will operate as a wet screen most of the time. However since it may operate without water sprays, emissions are calculated for this emissions point. PM Emissions factor calculated below.
- ^b Emission factors of screening, crushing, and conveying based on AP-42 Table 11.19.2-2. Alternate fuel PM factors assumed to have similar emissions as aggregate operation. Controlled emission factors are used since the moisture content of the raw material is estimated to be >1.5% (AP-42 basis for "controlled" emissions). Assume PM10 = PM2.5
- ^c Schenk Shredder, shredding at minimum of 50 tn/hr of biomass having diesel engine maximum size 630 (grinder) and 100 (screen) horse power. Total shredding requires 1400 hours. 100 and 630 HP Tier 3 engine emission factors stated below. SO₂ EF based on AP-42, 3.3-1 emission factor = 0.929gr/bhp^hhr-SO_x.

Engine Power	Tier	Year	CO	HC	NMHC +NO _x	NO _x	PM
(100 ≤ hp < 175)	Tier 2	2003	3.70	-	4.90	-	0.22
	Tier 3	2007	3.70	-	3.00	-	-T
(600 ≤ hp < 750)	Tier 2	2002	2.60	-	4.80	-	0.15
	Tier 3	2006	2.60	-	3.00	-	-T

	SO ₂ Inc./Dec.	NO _x Inc./Dec.	CO Inc./Dec.	VOC Inc./Dec.	PM/PM10 Inc./Dec.	PM2.5 ^a Inc./Dec.	Pb Inc./Dec.	Hg Inc./Dec.
	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(lbs)	(lbs)
Fugitives	0.85	2.79	3.25	2.79	1.81	1.71	0.00	0.00
Agricultural Film	0.00	0.00	0.00	0.00	0.00	0.00	-5.78	-1.47
Agricultural Waste	0.69	-2.84	8.19	0.76	2.75	1.37	-10.82	-1.20
Carpet-Derived Fuel	0.00	0.00	0.00	0.00	0.00	0.00	9.92	2.52
Clean Woody Biomass	1.20	-4.92	14.20	1.32	4.77	2.38	-18.99	-4.05
Manufacturer Reject Roofing Shingles	0.18	-20.01	0.00	1.03	0.00	0.00	20.55	-3.25
Preconsumer Paper	0.75	-3.08	8.87	0.82	2.98	1.49	-3.43	-2.93
Tire Derived Fuel	-0.08	-3.87	22.77	-0.08	-0.24	-0.12	-0.74	-5.76
On-Spec Used Oil	11.94	-2.07	-2.24	9.64	0.80	0.40	5.20	-0.71
Total	15.55	-34.00	55.05	16.28	12.86	7.23	-4.10	-16.85
PSD Threshold	40	40	100	40	25/15	10	1200	permits: 122 lb/yr

a. PM2.5 from Fugitives in Table 2. PM2.5 from alternative fuel firing conservatively estimated at 50% of fraction of PM.

Page 6. Item 3. Authorization.

We request to include the following statement:

Each alternative fuel trial is limited to no more than 60 operating days while co-firing coal. CEMEX may request additional time to complete a trial if operational problems prevent completion of the test within 60 days.

Page 6. Item 3a.

We request the language be changed to state:

- a. *Non-Chlorinated Agricultural Plastics*: This material consists of non-chlorinated, polyethylene (PE) low density polyethylene (LDPE) and/or high density polyethylene (HDPE) plastic....

Page 6. Item 3g.

We request the language be changed to remove the word ‘used’ to allow manufacturer reject carpet.

Page 6. Item 3h.

As mentioned above, we request off-specification oil be included. The gallon amount is not requested to change.

Page 7. Item 5.

We request that the acceptance criteria of on-specification oil include off-specification used oil.

Page 9. Item 13a. Compliance Tests.

Regarding PM testing, the impact of differing fuels is not a factor on the efficiency of the baghouse collection device. Efficiency of the baghouse is based on dust loading and dust loading is over 90 percent from raw materials.

Collaborative studies by EPA show that with competent test teams, the within-team Relative Standard Deviation (RSD) of a Method 5 test was 10.4 percent and the between-team RSD was 12.1 percent (see Attachment 1). More recently, ASME reported (see Attachment 1) that the RSD is from 5 to 11% and the accuracy of a Method 5 test (the departure of the average of three test runs from the true stack gas concentration) should be less than 14.7 percent.

Given that the precision and accuracy of one standard deviation of Method 5 test results are in the range of approximately 10-15 percent of the emission rate being measured, the impact of the fuel ash content should be within the measurement error of Method 5 and we request that particulate matter testing not be a requirement.

Page 9. Item 13b. Compliance Tests.

The impact of D/F testing is not a function of chlorine content of fuels but a function of the kiln system operation. The draft technical evaluation for this permit states, "At high temperatures and sufficient residence times, dioxins/furans can be destroyed. Pre-heater/pre-calciner kilns like that at the Brooksville South Cement Plant have high temperatures and sufficient retention times to destroy these organic compounds. The preheater/calciner design rapidly cools the exhaust gases, which prevents dioxin/furans from reforming."

Furthermore, the Evaluation states that TDF has been shown to reduce D/F emissions. According to a study by the Portland Cement Association (PCA)⁴:

"In 2008, PCA member companies completed a study on the impact of TDF firing on cement kiln air emissions. The study's data set included emission tests from 31 of the cement plants presently firing TDF. Dioxin-furan emission test results indicated that kilns firing TDF had emissions approximately one-third of those kilns firing conventional fuels – this difference was statistically significant. Emissions of particulate

Given that D/F is a function of kiln post-combustion conditions, not related to chlorine content, we request to not test for D/F emissions.

Page 9. Item 13c and d.

In follow up to our request (see attached) to only test for HCl or metals if the concentrations are above that of coal, we request that only the Raw Mill up conditions be tested. The Raw mill up conditions represent the normal operation mode of the system.

Page 9 Item 13c.

In follow up to our request (see attached) we request to remove fluorine analysis. While fluorine could be a precursor to a HAP of hydrogen fluoride, the EPA evaluation of HAP emissions (per 40 CFR 63, subpart LLL) of acidic gases resulted in only HCl emissions to be of concern. Furthermore, the portion of fluorine in fuels is a small fraction of that in the raw materials of which any potential HF generated would be well collected in the

alkaline materials throughout the kiln system. As such, we request to remove fluorine analysis.

Page 11. item 18.

We request to remove the statement:

The report shall also include the comparison of the contaminants in and emissions of the alternative fuel material with the contaminants in and emissions from traditional fuels to meet the legitimacy criteria in 40 CFR 241.3(d)(1).

The FDEP has not implemented this rule into its State Implementation Plan.

Page 9 of 11, item 13e.

Please see the attached articles (Attachment 2) regarding the extremely high efficiency of pesticide destruction in cement kilns. We provide this information in support of the request proposed in the email to Christy Devore on April 7, 2011, (page 9 of 11, item 13e).

Please feel free to contact me at (352) 377-5822 or mlee@kooglerassociates.com if you have any questions regarding this submittal. I sincerely appreciate your time and consideration for this innovative project.

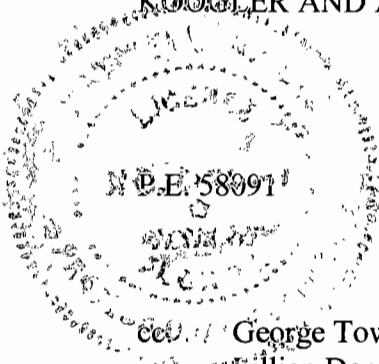
Regards,



Max Lee, Ph.D., P.E.
KOOGLER AND ASSOCIATES, INC.

Date

4/13/11



cc: George Townsend, CEMEX (email only)
Lillian Deprimo, CEMEX (email only)

Enc:

Attachment 1: References of EPA Method 5 evaluations



AN ASME REPORT

CRTD Vol. 60

Final Report

**Reference Method Accuracy and
Precision (ReMAP): Phase 1
Precision of Manual Stack Emission
Measurements**

Prepared by:

W. Steven Lanier
GE Energy and Environmental Research Corporation

Charles D. Hendrix
Statistical Consultant

under the auspices of:
American Society of Mechanical Engineers
Research Committee on Industrial and Municipal Waste

February 2001

Reference Method Accuracy and Precision (ReMAP Phase I) An Assessment of the Precision of EP A Manual Stack Emission Measurements

Executive Summary

This report documents results from the first phase of a study co-sponsored by the American Society of Mechanical Engineers (ASME) to assess the accuracy and precision of manual test methods adopted by the US Environmental Protection Agency (EP A) for determining the stack concentration of selected air pollutants. The program is entitled Reference Method Accuracy and Precision and is referred to by the acronym ReMAP. The Phase I effort addresses the precision of the selected measurement methods. The formal Purpose Statement for the program is:

"To determine the precision of pollutant emission measurements based on analysis of available simultaneous -sample test data which were generated using EPA Manual Reference Test Methods 5 and 5i (Particulate Matter), 23 (Dioxin and Furan), 26 (HCl), 29 (multi-metals), 101a and 101b (mercury) and 108 (arsenic) at a number of stationary air sources. "

As used in the ReMAP program, precision is defined as random error that inadvertently enters the measurement process. This error may enter at any stage of the measurement process including sample collection, sample recovery, or sample analysis. The impact of such errors is that measurement results deviate from the true stack concentration. Because these errors occur randomly, data from repeated application of any manual test method (to a hypothetical stack with a chosen average concentration of the selected pollutant) should result in a bell shaped frequency distribution. This distribution is centered about the chosen stack concentration but data are expected indicating measured concentrations both above and below the chosen stack value.

Precision of a measurement method is indicated by the horizontal spread of the bell curve. One common way to characterize the bell curve shape is to determine the estimated standard deviation (s) of the distribution. Alternately, the bell distribution also describes the range of measurement results anticipated from repeated application of the measurement method at the given concentration. Based upon the best estimate of the standard deviation, it is a simple matter to calculate other indicators of data quality that have direct practical significance. The ReMAP program selected two additional, directly derived parameters to characterize precision of manual methods:

1. The anticipated range for 99 out of 100 future single measurements. If the measurement method is repeatedly applied to a stack with a given concentration, this precision metric defines the upper and lower concentration bounds for 99% of individual measurements.
2. The anticipated range for 99 out of 100 future triplicate measurements. Since most environmental regulations define the reportable stack concentration as the average of three repeated test runs, this metric defines the anticipated range of results in triplicate (3 single time series) measurements due to random error in the measurement process.

For each of these precision metrics it is important to note the inherent assumption that the measurement method is being applied to a hypothetical stack with an average pollutant concentration that does not vary with time. In real-world applications, single and triplicate measurement results will indicate variation from both random errors and systematic errors (bias) in the measurement process as well as temporal variation in facility operation.

As noted, the primary objective of the ReMAP program is to characterize the bell shaped curve for each measurement method by first estimating the standard deviation s . The other two precision metrics are directly calculated from s . Specifically 99 out of 100 single measurements will fall within $\pm 2.54 s$ of the true concentration. The anticipated range for the average of repeated measurements comes progressively closer to the true concentration. More precisely, the anticipated range varies inversely with the square root of the number of measurements. Thus, if s is the standard deviation of anticipated single measurements, the anticipated range for 99 out of 100 future triplicate measurements will fall within $\pm 2.54 s / \sqrt{3}$ of the true concentration.

A central tenet of the ReMAP program is to determine how the precision of manual measurement methods varies with the concentration of the pollutant being measured. A constant measurement standard deviation might occur if the primary source of random error is an analytical process. A simple example might be the repeatability with which a technician can measure the weight gain on a particulate filter. The capabilities of the weighing scale do not significantly vary with the particulate weight gain. However, the magnitude of random errors associated with extraction and recovery of the sample from the stack might be expected to vary in proportion to stack concentration.

The technical effort of the ReMAP program is to estimate the standard deviation of selected EPA Measurement Reference Methods as a function of average stack concentration. ReMAP is not intended to validate any of the Reference Methods addressed herein nor is it to be used as a substitute for Method 301.

The concentration of pollutants released from industrial facilities must be assumed to vary with time. Accordingly, results from typical, single-train stack tests are of limited value for determination of the precision of a measurement method. Instead, estimation of method precision must be based on data from special tests where multiple sampling trains are used to simultaneously determine the stack pollutant concentration. Such multi-train tests minimize the impact of temporal and spatial (where probes are co-located) variations on the data and the results can be used to estimate the standard deviation of the particular measurement at the specific stack concentration.

The ReMAP program performed a careful assessment of the statistical analysis procedures required to estimate the precision of Manual Reference Methods using multi-train sampling data (see Appendix). To assure the quality of data used in the statistical analysis, an extensive effort was expended in gathering data from the original sources and carefully evaluating them to assure that consistent data reduction procedures were used.

Conceptually, the ReMAP statistical analysis procedure is straightforward. First, data from a multi-train test run are averaged to provide an estimate of the average concentration for the run (C_i). The standard deviation for the test run (S_i) is also calculated. Clearly, a calculated standard deviation from a single test using a dual sampling probe provides a relatively poor estimate of the true standard deviation of the method (s) at the true concentration (μ). However, after accounting for various biases, a significant array of data from multi-train tests should provide a reasonable basis for estimating the true standard deviation as a function of concentration. The ReMAP procedure is to assume that the standard deviation varies with concentration according to a power function relationship and then to fit the data to that equation using regression analysis.

Results from the regression analysis represent the best estimate available on the standard deviation of the measurement method at any given concentration. However, the ReMAP analysis procedure also provides for calculation of confidence intervals on the regression. These

confidence intervals define the upper and lower bounds for the regression line at the 95% confidence level. Based on the regression line and the confidence intervals, the various precision metrics can be determined for each Method as a function of concentration. Results from the analyses are summarized below.

EP A Method 5 and 5i for Particulate Matter - Front Half Only

Method 5 was one of the first EP A Reference Methods developed for stack sampling. There is a relatively large body of multi-train data indicating that the relative standard deviation (RSD) has minimal variation with concentration. Over a broad concentration range, RSD is predicted to remain between 5 and 11 %. There are certain data comparability concerns associated with the Method 5 precision analysis. However, assuming that the Method is applied to a stack with a particulate matter concentration less than 150 mg/dscm, the best available estimate is that RSD will be below 10%. Moreover, the influence of random error in the measurement process should result in the average of triplicate measurements deviating from the true average concentration by no more than about $\pm 14.7\%$ ($\pm 2.54 * 10\% / \sqrt{3}$).

Method 5i was specifically developed for application to stacks with particulate concentrations below 50 mg/dscm. The Method itself requires dual-train sampling and provides an upper limit on the allowable deviation between the simultaneous measurements. Thus the available data had been pre screened to eliminate test results with large standard deviation (i.e., > about 14% RSD). This prescreening, coupled with the relatively small concentration range for the data, resulted in the ReMAP analysis finding no statistically significant variation of standard deviation with concentration.

Based on a pooled analysis, the characteristic standard deviation for Method 5i was found to be 1.43 mg/dscm. Based on this best estimate of standard deviation, the ReMAP analysis indicates that 99 out of 100 Method 5i single measurements should deviate from the true concentration by no more than ± 3.68 mg/dscm. For triplicate measurements 99 out of 100 Method 5i data results should deviate from the true concentration by no more than ± 2.12 mg/dscm.

Method 23 for Dioxin and Furan

Data collected with Method 23 are used to report dioxin and furan emissions as either the total mass of tetra through octa chlorinated dioxin plus furan or as the toxic equivalent emission, adjusting the mass of each congener according to its toxicity relative to 2,3,7,8 TCDD. The individual 2,3,7,8 substituted dioxin and furan congeners in tetra through octa homologues are weighted by specific factors ranging from zero to 1.0 to determine the toxic equivalent of 2,3,7,8 TCDD.

The precision of Method 23 was assessed when data were reported in both forms. Even though the same data were used for both assessments, the ReMAP results suggest that the measurement precision varies according to how the data are reported. This implies that the random error associated with the sum of all the congener masses is different than random errors associated with the sum of weighted masses.

The ReMAP assessment of Method 23 was performed using a limited database of multi-train emissions data. For application of Method 23 for determination of total PCDD/PCDF mass, the ReMAP analysis found that RSD varied between about 6.3% and 20% for stack concentrations in the range of 2 to 27 ng/dscm. The following table presents the anticipated upper and lower bounds for 99 out of 100 Method 23 measurements as a function of the true stack concentration.

Table ES-1. Anticipated Range of Measurement Results Due to Random Error in Application of Method 23 for Total PCDD/PCDF Determination.

True Stack Concentration ng/dscm	99 out of 100 Single Measurements		99 out of 100 Triplicate Measurements	
	Lower Limit	Upper Limit	Lower Limit	Upper Limit
2	0.97	3.03	1.40	2.60
6	4.09	7.91	4.90	7.10
10	7.46	12.5	8.53	11.5
14	10.9	17.1	12.2	15.8
18	14.5	21.5	16.6	20.0
22	18.1	25.9	19.7	24.3
26	21.7	30.3	23.5	28.5

As noted, indicated measurement precision is different when Method 23 is used to determine concentration on a toxic equivalence basis. Specifically, the regression analysis found no statistically significant variation of standard deviation with concentration. Pooled analysis indicates that the best estimate of standard deviation is 0.027 ng ITEQ/dscm when the emission concentration is in the range of 0.02 to 9.9 ng ITEQ/dscm. This further indicates that 99 out of 100 future single measurements should fall with ± 0.069 ng ITEQ/dscm of the true concentration and 99 out of 100 triplicate measurements should fall within ± 0.04 ng ITEQ/dscm of the true concentration.

The absolute value of anticipated range for future Method 23 measurements (as ITEQ) are quite small in absolute terms but they are on the same order as regulatory emission limits being considered in some regions. As indicated above, the best estimate of standard deviation is 0.027 ng ITEQ/dscm. However, at 95% confidence, the standard deviation may be as large as 0.037 ng ITEQ/dscm and the potential range for 99 out of 100 future measurements might deviate from the true concentration by as much as ± 0.095 ng ITEQ/dscm. Relying upon a single measurement has the potential to create problematic findings. If emission limits were set at 0.095 ng ITEQ/dscm, to be assured of compliance at the 95% confidence level, measurement results could not exceed zero. Similarly, measurement results must be above 0.19 ng ITEQ/dscm to establish, with 95% confidence that the true stack concentration exceeded the emission limit.

Most regulations and permit limits establish compliance based on averaging results from triplicate measurements. The anticipated range for 99 out of 100 future triplicate measurements is reduced, relative to single measurements, by $\sqrt{3}$. Thus, compliance with an emission limit of 0.095 ng ITEQ/dscm is assured (at the 95% confidence level) when the triplicate average is at or below 0.04 ng ITEQ/dscm. Similarly, at 95% confidence, exceedence of the 0.095 ng ITEQ/dscm limit is assured when the three run average is above 0.15 ng ITEQ/dscm.

Method 26 for Hydrochloric Acid

ReMAP analysis of available data for Method 26 for HCl indicated that RSD is typically in the range of 5% to 10%. RSD does increase when the method is applied to stacks with very low

concentration. Table ES-2 summarized the anticipated upper and lower bounds for 99 out of 100 Method 26 measurements as a function of true stack HCl concentration.

Table ES-2. Anticipated Range of HCl Measurement Results Due to Random Error in Application of Method 26.

True Stack HCl Concentration mg/dscm	99 out of 100 Single Measurements		99 out of 100 Triplicate Measurements	
	Lower Limit	Upper Limit	Lower Limit	Upper Limit
1	0.65	1.35	0.80	1.20
5	3.72	6.28	4.26	5.74
10	7.76	12.2	8.71	11.3
20	16.1	23.9	17.7	22.3
50	41.9	58.1	45.3	54.7
100	85.8	114.2	91.8	108.2

Methods 29, 101a and 101b for Total Mercury

Several measurement methods have been developed for measurement of total emission concentration and for mercury speciation. The ReMAP analysis took all available multi-train mercury data collected using Methods 29, 101a and 101b but only used the data for total mercury concentration. The data analysis indicates that over the concentration range of 50 to 783 µg/dscm, the measurement method RSD varied from 9.6 to 12.4%. As concentration drops from 50 to 5 µg/dscm, the RSD is expected to rise from 12.4% to 15.4%. Table ES-3 summarizes the anticipated upper and lower bounds for 99 out of 100 mercury measurements using Methods 29 and 101 as a function of true stack total mercury concentration.

Table ES-3. Anticipated Range of Total Hg Measurement Results Due to Random Error in Application of Methods 29, 101a and 101b.

True Stack Hg Concentration µg/dscm	99 out of 100 Single Measurements		99 out of 100 Triplicate Measurements	
	Lower Limit	Upper Limit	Lower Limit	Upper Limit
4	2.19	5.81	2.96	5.04
10	5.96	14.0	7.70	12.3
25	16.0	34.0	19.3	30.2
50	33.4	66.6	40.4	59.6
75	51.3	98.7	61.7	88.7
100	69.5	130.5	82.4	117.6

Method 29 for Multi-Metals

Method 29 is also used for measurement of several other metal emissions. Precision analysis was completed for six other metals including antimony, arsenic, beryllium, cadmium, chromium, and

lead. With the exception of cadmium, the analysis indicates that these metals behave similarly with respect to measurement method precision. A composite analysis was performed for the five similarly behaving metals and the results, 0 indicate that use of Method 29 provides an RSD that varies between 13 and 18% when the individual metal concentrations are between about 20 and 100 $\mu\text{g}/\text{dscm}$. Table ES-4 summarizes the anticipated upper and lower bounds for 99 out of 100 Sb, As, Be, Cr, and Pb measurements using Methods 29 as a function of true stack total metal concentration.

As regards cadmium measurements using Method 29, the analysis indicates that standard deviation is a weaker function of concentration, at least at higher concentration ranges. The best estimate of RSD is 9.1 % when cadmium concentration is 80 $\mu\text{g}/\text{dscm}$ and 18.7 % when the concentration drops to 20 $\mu\text{g}/\text{dscm}$. However, at 5 $\mu\text{g}/\text{dscm}$, predicted RSD is 38.6% and at 1.4 $\mu\text{g}/\text{dscm}$ RSD is predicted to exceed 75%.

ES-6

Table ES-4. Anticipated Range of Sb, As, Be, Cr, and Pb Measurement Results Due to Random Error in Application of Methods 29 (Composite Analysis).

True Stack Sb, As, Be, Cr, or Pb Concentration $\mu\text{g}/\text{dscm}$	99 out of 100 Single Measurements		99 out of 100 Triplicate Measurements	
	Lower Limit	Upper Limit	Lower Limit	Upper Limit
5	2.16	7.84	3.36	6.64
20	11.0	29.0	14.8	25.2
40	24.0	56.0	30.8	49.2
60	37.6	82.4	47.1	72.9
80	51.5	108.5	63.6	96.4
100	65.7	134.3	80.2	119.8



**Quality Assurance
Handbook for
Air Pollution
Measurement
Systems:
Volume III. Stationary
Sources Specific
Methods**

Section 3.16

Section 3.4

METHOD 5--DETERMINATION OF PARTICULATE EMISSIONS
FROM STATIONARY SOURCES

OUTLINE

<u>Section</u>	<u>Documentation</u>	<u>Number of Pages</u>
SUMMARY	3.4	1
METHOD HIGHLIGHTS	3.4	15
METHOD DESCRIPTION		
1. PROCUREMENT OF APPARATUS AND SUPPLIES	3.4.1	15
2. CALIBRATION OF APPARATUS	3.4.2	22
3. PRESAMPLING OPERATIONS	3.4.3	20
4. ON-SITE MEASUREMENTS	3.4.4	19
5. POSTSAMPLING OPERATIONS	3.4.5	15
6. CALCULATIONS	3.4.6	10
7. MAINTENANCE	3.4.7	3
8. AUDITING PROCEDURE	3.4.8	7
9. RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY	3.4.9	1
10. REFERENCE METHOD	3.4.10	6
11. REFERENCES	3.4.11	2
12. DATA FORMS	3.4.12	21

SUMMARY

This method, when used in conjunction with Methods 1, 2, 3, and 4, is applicable for the determination of particulate emissions from stationary sources.

A gas sample is extracted isokinetically from the stack. Particulate matter is collected on an out-of-stack, glass fiber filter, maintained at $120^{\circ} \pm 14^{\circ}\text{C}$ ($248^{\circ} \pm 25^{\circ}\text{F}$) or at a temperature specified by an applicable subpart of the standards or approved by the administrator. The mass of particulate matter, which includes any material that condenses at or above the specified filter temperature, is measured gravimetrically after removal of uncombined water.

The Method Description which follows is based on the Reference Method that was promulgated on August 18, 1977. Results of an initial collaborative test program indicated the need for more specific quality controls and a better defined Reference Method, which resulted in the expansion and revisions incorporated in the August 18, 1977 promulgation. As a result, competence of the tester becomes the primary factor affecting the precision of Method 5. Results of the most recent collaborative test program, conducted with competent test teams, showed a within-laboratory deviation (standard deviation percent of mean value) of 10.4% and a between laboratory deviation of 12.1%.²

The main documents used in preparing the description and in detailing calibration and maintenance procedures are references 1, 3, and 4 (Section 3.4.11). Data forms are provided in Section 3.4.12 for the convenience of the Handbook users.

11.0 REFERENCES

1. Standards of Performance for New Stationary Sources, Federal Register, Vol. 42, No. 160. August 18, 1977.
2. Hamil, H. F. and R. E. Thomas. Collaborative Study of Particulate Emissions Measurements by EPA Methods 2, 3, and 5 using Paired Particulate Sampling Trains. EPA-600/4-76-014. Environmental Protection Agency, Research Triangle Park, N.C., March 1976.
3. Martin, R. M. Construction Details of Isokinetic Source Sampling Equipment. Publication No. APTD-0581. Air Pollution Control Office, EPA, Research Triangle Park, N.C., 1971.
4. Rom, J. J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Pub No. APTD-0576. Office of Air Programs, EPA, Research Triangle Park, N.C., 1972.
5. Midgett, M. R. The EPA Program for the Standardization of Stationary Source Emission Test Methodology, A Review. EPA-600/4-76-044. Environmental Protection Agency, Research Triangle Park, N.C., August 1976.

Additional References

Smith, Franklin, and Denny E. Wagoner. Guidelines for Development of a Quality Assurance Program: Volume IV - Determination of Particulate Emissions from Stationary Sources. Contract No. 68-02-1234, EPA-650/4-74-005-d. Research Triangle Institute, Research Triangle Park, N.C., August 1974.

Highlights of August 18, 1977, Revisions to EPA Reference Methods 1-8. Entropy Environmentalists, Inc. Research Triangle Park, N.C. (for EPA).

USEPA. Public Comment Summary: Revisions to Reference Methods 1-8 in Appendix A of Standards of Performance for New Stationary Sources. Environmental Protection Agency, Research Triangle Park, N.C., June 1977.

Vollara, Robert F. An Evaluation of the Current EPA Method 5 Filtration Temperature - Control Procedure. Environmental Protection Agency, Research Triangle Park, N.C.

Attachment 2: Reference Articles on Pesticide Destruction

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/envsci

Review

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

Kåre Helge Karstensen^{a,*}, Nguyen Khac Kinh^b, Le Bich Thang^c, Pham Hung Viet^d,
 Nguyen Dinh Tuan^e, Doan Thi Toi^f, Nguyen Hoang Hung^g, Tao Manh Quan^h,
 Luong Duy Hanhⁱ, Doan Huu Thang^j

^a The Foundation for Scientific and Industrial Research (SINTEF), P.O. Box 124, N-0314 Oslo, Norway

^b Ministry of Natural Resources and Environment, Department of EIA and Appraisal, 83 Nguyen Chi Thanh, Hanoi, Viet Nam

^c Vietnam Environmental Protection Agency, 67 Nguyen Du, Hanoi, Viet Nam

^d Hanoi University of Science, Research Centre for Environmental Technology and Sustainable Development, 334 Nguyen Trai, Hanoi, Viet Nam

^e Ho Chi Minh City Environmental Protection Agency, 23 Tran Phu, Ward 4, Ho Chi Minh City, Viet Nam

^f Department of Natural Resources and Environment, 244 Dien Bien Phu Street, Ho Chi Minh City, Viet Nam

^g Department of Natural Resources and Environment, 260 Quoc Lo, Bien Hoa City, Dong Nai, Viet Nam

^h Department of Natural Resources and Environment, Huynh Van Nghe, Thu Dao Mot, Binh Duong, Viet Nam

ⁱ Department of Natural Resources and Environment, 130 Ly Thuong Kiet, Vung Tau, Viet Nam

^j Department of Natural Resources and Environment, 1226 Nguyen Trung, Rach Gia Bo, Kien Giang, Viet Nam

ARTICLE INFO

Published on line 21 July 2006

Keywords:

Hazardous chemicals

POPs

Disposal

Co-processing

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 99.9999969% for Fenobucarb and better than 99.9999832% 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.

© 2006 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +47 930 59 475; fax: +47 2206 7350.

E-mail address: khk@sintef.no (K.H. Karstensen).

1462-9011/\$ – see front matter © 2006 Elsevier Ltd. All rights reserved.

doi:10.1016/j.envsci.2006.05.005

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; IPPC, 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 m³ 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, CO₂, O₂, NO_x 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/ N m^3 with coal only and 0.015, 0.053 and 0.068 ng I-TEQ/ 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 CO_2 , O_2 and 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.

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, O₂, CO and NO_x; the preheater outlet gas for temperature, O₂, CO and NO_x and the stack outlet gas for temperature, O₂, CO, CO₂, NO, NO₂, SO₂, HCl, NH₃, H₂O and volatile organic carbon (VOC). The main stack is 122 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 Hudén (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 C₁₂H₁₇NO₂ (Fig. 1).

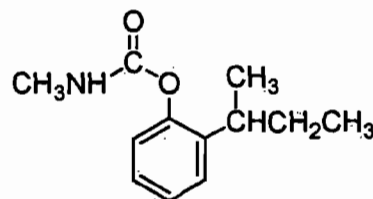


Fig. 1 – Chemical structure of Fenobucarb.

Fipronil has a molecular weight of 437.2 with the sum molecular formula C₁₂H₄Cl₂F₆N₄OS 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 m³ steel tank for receiving, blending and feeding of the insecticide mix was build 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 banded concrete construction for spill recovery. The insecticide mix was pumped from the tank through stainless steel pipes

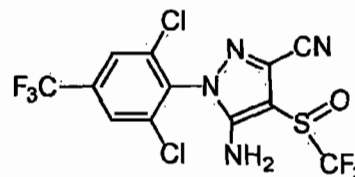


Fig. 2 – Chemical structure of Fipronil.

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. when 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/m³, 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 (Nm³/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/m³)

	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 (SiO₂ 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 m³. 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% O₂)

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

Table 3 – Gaseous compounds (mg/N m³)

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

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 m³ 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 SO₂ was less than 1% of the emission limit value (225 mg/N m³) and independent of the insecticide disposal. Ninety-nine percentages of the sulphur oxides emitted from cement kilns is in the form of SO₂ and originates mainly from sulphides and organically bound sulphur in fuels and raw materials (Oss and Padovani, 2003).

The reason for the high NO_x levels during the test burn was due to high heat input through the main flame due to wrong information about heat content of the 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_x levels. The NO_x 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_x emissions from cement kilns are NO, the rest is NO₂ (Oss and Padovani, 2003).

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

4.5.4. Results of solid particles and metals

The concentration of dust was 33 and 20 mg/N m³ 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 mg/N m³. 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 mg/kg under baseline and test burn conditions, respectively; the fluorine was <0.40 mg/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 needs 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 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 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.

REFERENCES

- Ahling, B., 1979. Destruction of chlorinated hydrocarbons in a cement kiln. *Environ. Sci. Technol.* 13, 1377.
- Balbo, M., Francois, A., de Ladebat, H., Mosnier, F., 1998. Cement kiln incineration—a viable waste management solution. *International Directory of Solid Waste Management. The ISWA Yearbook 1997*, ISBN 1-873936-73-5.
- Basel Convention, 1989. In: *Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal Adopted by the Conference of the Plenipotentiaries, Secretariat of the Basel Convention*, 13-15 Chemin des Anemones, CH-1219 Chatelaine, Geneva, Switzerland.
- Basel Convention, 2006. General technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs). Draft unedited Version: 7 April 2006. <http://www.basel.int/techmatters/techguid/frsetmain.php?topicId=0>.
- Benestad, C., 1989. Incineration of hazardous waste in cement kilns. *Waste Manage. Res.* 7, 351.
- Branscome, M., Westbrook, W., Mourmighan, R., Bolstad, J., Chehaske, J., 1985. Summary of testing at cement kilns co-firing hazardous waste. In: *Proceedings of the Eleventh Annual Research Symposium on Incineration and Treatment of Hazardous Waste*. EPA 600/9-85-028, p. 199.
- Brevik, K., Alcock, R., Li, Y.-F., Bailey, R.E., Fiedler, H., Pacyna, J.M., 2004. Primary sources of selected POP's: Regional and global scale emission inventories. *Environ. Pollut.* 128, 3-16.
- Cembureau, 2004. <http://www.cembureau.be/Brussels>.
- Chadbourne, J.F., 1997. Cement kilns. In: Freeman, H.M. (Ed.), *Standard Handbook of Hazardous Waste Treatment and Disposal*. McGraw-Hill, ISBN 0-07-022044-1.
- Decision 155, 1999. Decision of the Prime Minister on the promulgation of regulation on hazardous waste management in Vietnam. No. 155/1999/QD-TTg.
- De Vito, M.J., Birnbaum, L.S., 1995. Dioxins: Model chemicals for assessing receptor-mediated toxicity. *Toxicology* 102, 115-123.
- DoSTE (Department of Science, Technology Environment), 1998. Scientific report on the assessment of pesticide use in Ho Chi Minh City. *Environmental Problems and Solutions*, vol. 1.
- Duda, W.H., 1985. *Cement Data Book*. Bauverlag GmbH, Berlin.
- FAO, 1999. In: *Prevention and Disposal of Obsolete and Unwanted Pesticide Stocks in Africa and the Near East—Fourth Consultation Meeting*, Food and Agriculture Organization of the United Nations, Viale delle Terme di Caracalla, 00100 Rome.
- FAO, 2001a. *Baselines study on the problem of obsolete pesticide stocks*. FAO Pesticide Disposal Series 9. Food and Agriculture Organization of the United Nations, Viale delle Terme di Caracalla 00100, Rome, Italy.
- FAO, 2001b. *The ticking time bomb: toxic pesticide waste dumps*. Press release, Food and Agriculture Organization of the United Nations, Viale delle Terme di Caracalla, 00100 Rome.
- Federal Register, 1999. *National Emissions Standards for Hazardous Air Pollutants – US EPA – Final Rule. Part II*, 40 CFR Part 60, September 30, pp. 52827-53077.
- Federal Register, 2000. *National Emissions Standards for Hazardous Air Pollutants – US EPA – CFR Promulgated Test Methods (TM)*, vol. 65, No. 201, October 17.
- Gabrielsen, G.W., Knudsen, L.B., Verreault, J., Push, K., Muir, D.D.C., Letcher, R.J., 2004. Halogenated organic contaminants and metabolites in blood and adipose tissue of Polar Bears from Svalbard. Report to the Norwegian Pollution Control Authority, ISBN 82-7655-490-3.
- Garg, 1990. Emissions testing of a wet cement kiln at Hannibal Missouri. US EPA 530/SW-91-017, Washington, DC.
- Godduhn, A., Duffy, L.K., 2003. Multi-generation health risks of persistent organic pollution in the far north: use of the precautionary approach in the Stockholm Convention. *Environ. Sci. Policy* 6, 341-352.
- Gupta, P.K., 2004. Pesticide exposure—Indian scene. *Toxicology* 198, 83-90.
- HCMC, 2002. *Ho Chi Minh City Environmental Strategy*. Environmental Resource Management. Department of Natural Resources and Environment, 244 Dien Bien Phu Street, Ho Chi Minh City.
- Huden, G.H., 1990. Pesticide disposal in a cement kiln in Pakistan—a pilot project. In: *Pacific Basin Conference on Hazardous Waste*, East-West Center, Honolulu, November 12-14.
- Hung, D.Q., Thiemann, W., 2002. Contamination by selected chlorinated pesticides in surface waters in Hanoi, Vietnam. *Chemosphere* 47, 357-367.
- IPPC Integrated Pollution Prevention and Control (IPPC)—European Commission, December 2001. Reference document on Best Available Techniques in the Cement and Lime manufacturing industries. <http://www.jrc.es/pub/english.cgi/>.
- Jobling, S., Casey, D., Rodgers-Gray, T., Oehlmann, J., Schulte-Oehlmann, U., Pawlowski, S., Baunbeck, T., Turner, A.P., Tyler, C.R., 2004. Comparative responses of molluscs and fish to environmental estrogens and an estrogenic effluent. *Aquat. Toxicol.* 66, 207-222.
- Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POPs): State of the science. *Environ. Pollut.* 100 (1-3), 209-221.
- Karstensen, K.H., 1994. Burning of hazardous wastes as co-fuel in a cement kiln—does it affect the environmental quality of cement?—leaching from cement based materials. *Studies in Environmental Science: Environmental Aspects of Construction with Waste Materials*, vol. 60. Elsevier, Amsterdam, The Netherlands, ISBN 0-444-81853-7.
- Karstensen, K.H., 1998a. Benefits of incinerating hazardous wastes in cement kilns. In: *Third Consultation Meeting on Prevention and Disposal of Obsolete and Unwanted Pesticide Stocks in Africa and the Near East*, FAO Pesticide Disposal Series 6, Food and Agriculture Organization of the United Nations, Rome.
- Karstensen, K.H., 1998b. Disposal of principal organic hazardous compounds in cement kilns—an alternative to dedicated

- incinerators? In: Proceedings of the Fifth International HCH and Pesticides Forum, Bilbao, June 25-27.
- Karstensen, K.H., 2001a. Incineration of principal organic hazardous compounds and hazardous wastes in cement kilns— which requirements should be fulfilled? In: First Continental Conference for Africa on the Environmentally Sound Management of Unwanted Stocks of Hazardous Wastes and their Prevention. Basel Convention, Rabat, January 8-12.
- Karstensen, K.H., 2001b. Disposal of obsolete pesticides in cement kilns in developing countries— lessons learned and how to proceed. In: Proceedings of the Sixth International HCH and Pesticide Forum, Poznan, Poland, March 20-22.
- Karstensen, K.H., Wormstrand, E., Weholt, Ø., Hall, T., Wenborn, M., Faircloth, P., Lindskog, E., 2003a. Master plan for hazardous waste management in Ho Chi Minh City, Dong Nai, Binh Duong and Ba Ria Vung Tau, Department of Natural Resources and Environment, 244 Dien Bien Phu Street, Ho Chi Minh City, 16 January.
- Karstensen, K.H., Ringstad, O., Kvernheim, A.L., 2003b. Inventory and assessment of principal organic hazardous compound stocks and evaluation of disposal capacity for hazardous chemicals in Vietnam. Ministry of Natural Resources and Environment, Vietnam Environmental Protection Agency, 67 Nguyen Du, Hanoi, November.
- Karstensen, K.H., 2004. Formation and release of POPs in the cement industry. *Organohalogen Compd.* 66 ISBN 3-928379-30-5.
- Karstensen, K.H., 2006a. Thermal destruction of obsolete pesticides. In: Proceedings of Eighth International HCH and Pesticides Forum for Central European and EECCA Countries, Sofia, Bulgaria, May 26-28.
- Karstensen, K.H., 2006b. Formation and Release of POPs in the Cement Industry, 2nd ed. Report to the World Business Council for Sustainable Development. <http://www.wbcscement.org/>.
- Kawata, K., Mukai, H., Yasuhara, A., 1995. Monitoring of pesticides in air by gas chromatography mass spectrometry and the use of quartz fibre wool and activated carbon for sampling. *J. Chromatogr. A* 710, 243-250.
- Laubert, J.D., 1982. Burning chemical wastes as fuels in cement kilns. *J. Air Pollut. Contr. Assoc.* 32 (7), 771-776.
- Laubert, J.D., 1987. Destruction and disposal of waste PCB. In: Waid, J.S. (Ed.), *PCBs and the Environment*. CRC Press, USA.
- Mac Donald, L.P., Skinner, D.J., Hopton, F.J., Thomas, G.H., 1977. Burning waste chlorinated hydrocarbons in a cement kiln. Environment Canada, Report EPS 4/WP/77-2.
- McDonal, T.A., 2002. A perspective on the health risks of PBDES. *Chemosphere* 46, 745-755.
- Minh, N.H., Someya, M., Minh, T.B., Kunisue, T., Iwata, H., Watanaba, M., Tanabe, S., Viet, P.H., Tuyen, B.C., 2004. Persistent organochlorine residues in human breast milk from Hanoi and Ho Chi Minh City Vietnam. *Environ. Pollut.* 129, 431-441.
- Oss, H.G., Padovani, A.C., 2003. Cement manufacture and the environment. *J. Ind. Ecol.* 7 (1), 93-125.
- Quyen, P.B., Nhan, D.D., San, N.V., 1995. Environmental pollution in Vietnam: analytical estimation and environmental priorities. *Trends Anal. Chem.* 14 (8), 383-388.
- Schimpf, W.A., 1990. Disposal of pesticides and chemical waste in a cement kiln in Malaysia. In: Proceedings of the Pesticide Disposal Conference, Niamey, Niger, January 21-26.
- Schimpf, W.A., 1998. Disposal of obsolete pesticides in a cement kiln in Tanzania— experience with the incineration of dinitro-o-cresol in a cement rotary cylindrical kiln in a developing country. In: Proceedings of the Fifth International HCH and Pesticides Forum, Bilbao, June 25-27.
- Science in Africa, 2002. Stockpiles of obsolete pesticides in Africa higher than expected. <http://www.scienceinAfrica.co.za/2002/october/pests.htm>.
- Stobiecki, S., Fuszara, E., Baron, L., Silowiecki, A., Stobiecki, T., 2003. Disposal of obsolete pesticides as an alternative fuel in cement kiln. In: Proceedings of the Seventh International HCH and Pesticides Forum, Kiev, June 5-7.
- Suderman, R.W., Nisbet, M.A., 1992. Waste derived fuel as a supplementary energy source at the Woodstock Cement Plant. Environment Canada, Report EPS 3/UP/6.
- UNECE, 1998. The Aarhus Protocol on Persistent Organic Pollutants. United Nations Economic Commission for Europe. http://www.unece.org/env/lrtap/POP's_h1.htm.
- UNEP, 2001. The Stockholm Convention on Persistent Organic Pollutants. United Nations Environmental Programme. <http://www.chem.unep.ch/sc/default.htm>.
- UNEP, 2004. Review of the Emerging, Innovative Technologies for the Destruction and Decontamination of POP's and the Identification of Promising Technologies for Use in Developing Countries. <http://www.unep.org/stapgef>.
- Vallack, H.W., Bakker, D.J., Brandt, I., Brorstrom-Lunden, E., Brouwer, A., Bull, K.R., Gough, C., Guardans, R., Holoubek, I., Jansson, B., Koch, R., Kuylenstierna, J., A. LeclouxMackay, D., McCutcheon, P., Mocarelli, P., Taalman, R.D.F., 1998. Controlling persistent organic pollutants— what next? *Environ. Toxicol. Pharmacol.* 6 (3), 143-175.
- Viken, W., Waage, P., 1983. Treatment of hazardous waste in cement kilns within a decentralised scheme: the Norwegian experience. *Industry and Environment*, vol. 4. UNEP.
- Vilchez, J.L., Prieto, A., Araujo, L., Navalon, A., 2001. Determination of fipronil by solid phase microextraction and gas chromatography mass spectrometry. *J. Chromatogr. A* 919, 215-221.
- WHO, 2002. The WHO recommended classification of pesticides by hazard and guidelines to classification, ISBN 92-4-154564X.
- WHO, 2003. Health risks of persistent organic pollutants from long range transboundary air pollution. <http://www.euro.who.int>.
- World Bank, 2004. Vietnam Environment Monitor 2004. World Bank.

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

Kåre Helge Karstensen

The Foundation for Scientific and Industrial Research (SINTEF), P. O. Box 124, N-
0314 Oslo, Norway

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.

*Tel: +47-930-59-475; fax: +47-2206-7350 E-mail address: khk@sintef.no

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°C to 1000°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°C to 980°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°C to 690°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°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°C to 1100°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°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°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 $\mu\text{g}/\text{m}^3$. 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, Chloroethanes, 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 SO₂ 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 m³ 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 were 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 Nm³/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 Ib) 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 where 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, CO₂, O₂, 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 m³ 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 plant 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, Fenitrothion, 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, Fenitroton, 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 $\mu\text{g}/\text{m}^3$) 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 were 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 than 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 Dneestr was evaluated. The NATO feasibility study however, recommended not to continue 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 encouraging 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 have 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 CO₂, O₂ 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 where the objective was to carry out a test burn to investigate if the cement kiln was able to co-process hazardous wastes in an irreversible and environmentally 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.

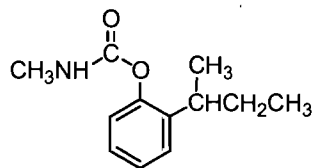


Fig. 1 Chemical structure of Fenobucarb.

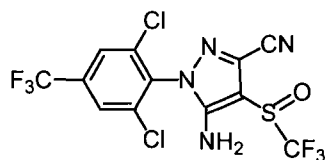


Fig. 2 Chemical structure of Fipronil.

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/Nm³ (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 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, where 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 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.

References

- Ackerman, D.G., Fisher, H.J., Johnson, R.J., Maddalone, R.F., Matthews, B.J., Moon, E.L., Scheyer, K.H., Shih, C.C. and Tobias, R.F., 1978. At Sea incineration of Herbicide Orange onboard the M/T Vulcanus. US Environmental Protection Agency, EPA-600/2-78-086.
- Ahling, B., 1979. Destruction of chlorinated hydrocarbons in a cement kiln. *Environmental Science and technology*, 13, 1377.
- Atkins, P.R., 1972. The pesticide manufacturing industry – current waste treatment and disposal practices. US EPA Project # 12020 FYE.
- Basel Convention, 1989. Basel Convention on the control of transboundary movements of hazardous wastes and their disposal adopted by the conference of the plenipotentiaries. Secretariat of the Basel Convention, 13 - 15 Chemin des Anemones, CH - 1219 Chatelaine, Geneva, Switzerland.
- Benestad, C., 1989. Incineration of hazardous waste in cement kilns. *Waste Management Research*, 7, 351.
- Branscome, M., Westbrook, W., Mournighan, R., Bolstad, J., and Chehaske, J., 1985. Summary of testing at cement kilns co-firing hazardous waste. In *Incineration and treatment of hazardous waste: Proceedings of the Eleventh Annual Research Symposium*, EPA 600/9-85-028, 199.

Brevik, K., Alcock, R., Yi-Fan Li, Bailey, R.E., Fiedler, H. and Pacyna, J.M., 2004. Primary sources of selected POP's: regional and global scale emission inventories. *Environmental Pollution*, 128, 3-16.

Brunner, C.R., 1993. *Hazardous Waste Incineration*. ISBN 0-07-008595-1. McGraw-Hill, Inc., New York.

Cementos Boyaca, 1999. Pesticide contaminated soils co-processing - Nobsa Plant experience. Internal report.

Chadborne, J.F., 1997. *Cement Kilns*. Freeman, H.M. (ed.), 1997. *Standard Handbook of Hazardous Waste Treatment and Disposal*. ISBN 0-07-022044-1. McGraw-Hill.

Council Directive, 2000. Council Directive 2000/76/EC on the Incineration of Waste. *Official Journal of the European Communities, Brussels, Official Journal L 332, 28/12/2000*.

Dempsey, C.R., and Oppelt, E.T., 1993. *Incineration of Hazardous Waste: A Critical Review Update*. *Air & Waste*, Vol. 43, 25-73.

De Vito, M.J. and Birnbaum, L.S., 1995. Dioxins: model chemicals for assessing receptor-mediated toxicity. *Toxicology*, 102, 115-123.

Duda, W.H., 1985. Cement Data Book. Bauverlag Gmbh, Berlin.

Duvall, D.W. and Rubey, W.A., 1976. Laboratory evaluation of high temperature destruction of Kepone and related pesticides. US Environmental Protection Agency, EPA-600/2-76-299.

FAO, 1999. Prevention and disposal of obsolete and unwanted pesticide stocks in Africa and the Near East – Fourth consultation meeting. Food and Agriculture Organization of the United Nations, Viale delle Terme di Caracalla, 00100 Rome.

FAO, 2001a. Baseline study on the problem of obsolete pesticide stocks. FAO Pesticide Disposal Series 9. Food and Agriculture Organization of the United Nations, Viale delle Terme di Caracalla, 00100 Rome, Italy.

FAO, 2001b. The ticking time bomb: toxic pesticide waste dumps. Press release, Food and Agriculture Organization of the United Nations, Viale delle Terme di Caracalla, 00100 Rome, 9 May.

Federal Register, 1999. National Emissions Standards for Hazardous Air Pollutants – US EPA – Final Rule. Part II, 40 CFR Part 60, September 30, 52827-53077.

Ferguson, T.L., Bergman, F.J., Cooper, G.R., Li, R.T. and Honea, F.I., 1975. Determination of incinerator operating conditions necessary for safe disposal of pesticides. US Environmental Protection Agency, EPA-600/2-75-041.

- Ferguson, T.L. and Wilkinson, R.R., 1984. Treatment and disposal of pesticide wastes. Krueger, R.F. and Seiber, J.N. (eds.). Am. Chem. Soc. Symposium Series 259, 181-191.
- Freeman, H.M. (ed.), 1997. Standard Handbook of Hazardous Waste Treatment and Disposal. ISBN 0-07-022044-1. McGraw-Hill.
- Gabrielsen, G.W, Knudsen, L.B., Verreault, J., Push, K., Muir, D.D.C. and Letcher, R.J., 2004. Halogenated organic contaminants and metabolites in blood and adipose tissue of Polar Bears from Svalbard. Report to the Norwegian Pollution Control Authority. ISBN 82-7655-490-3.
- Garg, 1990. "Emissions testing of a wet cement kiln at Hannibal Missouri". EPA 530/SW-91-017, US EPA, Washington DC.
- Godduhn, A. and Duffy, L.K., 2003. Multi-generation health risks of persistent organic pollution in the far north: use of the precautionary approach in the Stockholm Convention. *Env. Science & Policy*, 6, 341-352.
- Gupta, P.K., 2004. Pesticide exposure – Indian scene. *Toxicology*, 198, 83-90.
- Hall, F.D., Kemner, W.F. and Staley, L.J., 1983. Evaluation of feasibility of incinerating hazardous wastes in high temperature industrial processes. 8th Annual Research Symposium, Incineration and treatment of hazardous waste. US Environmental Protection Agency, EPA-600/9-83-003.

Huden, G. H., 1990. Pesticide disposal in a cement kiln in Pakistan – A pilot project. Pacific Basin Conference on Hazardous Waste, East-West Center, Honolulu, November 12-14.

Integrated Pollution Prevention and Control (IPPC) – European Commission, 2001. “Reference document on Best Available Techniques in the Cement and Lime manufacturing industries”. <http://www.jrc.es/pub/english.cgi/>

Jannerup, H. E., 1998. “Destruction of obsolete pesticides in Mozambique”. 5th International HCH and Pesticides Forum, Bilbao, June 25-27.

Jobling, S., Casey, D., Rodgers-Gray, T., Oehlmann, J., Schulte-Oehlmann, U., Pawlowski, S., Baunbeck, T., Turner, A.P., and Tyler, C.R., 2004. Comparative responses of molluscs and fish to environmental estrogens and an estrogenic effluent. *Aquatic Toxicology*, 66, 207-222.

Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POP's): state of the science. *Environmental Pollution* 100 (1-3), 209–221.

Karstensen, K. H., 1994. Burning of Hazardous Wastes as Co-Fuel in a Cement Kiln - Does it Affect the Environmental Quality of Cement? - Leaching from Cement Based Materials. *Studies in Environmental Science* 60, "Environmental Aspects of Construction with Waste Materials", Elsevier, Amsterdam, Netherlands.

Karstensen, K. H., 1998a. Benefits of incinerating hazardous wastes in cement kilns. FAO Pesticide Disposal Series 6, Prevention and disposal of obsolete and unwanted pesticide stocks in Africa and the Near East, Third consultation meeting, Food and Agriculture Organization of the United Nations, Rome, 1998.

Karstensen, K. H., 1998b. Disposal of principal organic hazardous compounds in cement kilns – An alternative to dedicated kilns? 5th International HCH and Pesticides Forum, Bilbao, 25-27 June.

Karstensen, K.H., 2000. Disposal of obsolete pesticides in Mozambique - Review report. DANIDA, Denmark.

Karstensen, K. H., 2001a. Incineration of principal organic hazardous compounds and hazardous wastes in cement kilns – Which requirements should be fulfilled? First Continental Conference for Africa on the Environmentally Sound Management of Unwanted Stocks of Hazardous Wastes and their Prevention, Basel Convention, Rabat, 8-12 January.

Karstensen, K. H., 2001b. Disposal of obsolete pesticides in cement kilns in developing countries – Lessons learned and how to proceed. 6th International HCH and Pesticide Forum, Poznan, Poland, 20-22 March.

Karstensen, K. H., Wormstrand, E., Weholt, Ø., Hall, T., Wenborn, M., Faircloth, P. and Lindskog, E., 2003a. Master plan for hazardous waste management in Ho Chi

Minh City, Dong Nai, Binh Duong and Ba Ria Vung Tau, 16 January. Department of Natural Resources and Environment, 244 Dien Bien Phu Street, Ho Chi Minh City.

Karstensen, K. H., Ringstad, O. and Kvernheim, A.L., 2003b. Inventory and assessment of obsolete pesticide stocks and evaluation of disposal capacity for hazardous chemicals in Vietnam, November. Ministry of Natural Resources and Environment, Vietnam Environmental Protection Agency, 67 Nguyen Du, Hanoi.

Karstensen, K. H., 2004a. Formation and release of POP's in the cement industry. Report to the World Business Council for Sustainable Development, <http://www.wbcsd.org/web/projects/cement/pop-summary.pdf>.

Karstensen, K. H., 2004b. Destruction of organic obsolete pesticides in Moldova - Evaluation of the suitability of the cement kiln in Rezina. NATO Public Diplomacy Division – Collaborative Programmes Section, Brussels, June.

Karstensen, K. H., 2004c. Evaluation of the Feasibility of Using a Cement Kiln for Thermal Treatment of Organic Hazardous Wastes in South Vietnam. Submitted to Jour. of Haz. Materials for publication.

Kennedy, M.V., Stojanovic, B.J. and Shuman, Jr., F.L., 1969. Chemical and thermal methods for disposal of pesticides. Residue Reviews 29, 89-104.

Lauber, J.D., 1982. "Burning chemical wastes as fuels in cement kilns". Jour. of the Air Pollution Control Association, 32, 7, 771-776.

Lauber, J.D., 1987. Disposal and destruction of waste PCB. PCBs and the Environment, Edited by Waid, J.S. CRC Press, USA.

Lee, C.C., Huffman, G.L., and Mao, Y.L., 2000. Regulatory framework for the thermal treatment of various waste streams. Journal of Hazardous Materials, A76, 13-22.

Leighton, I.W. and Feldman, J.B., 1975. Demonstration test burn on DDT in GE liquid injection incinerator. US Environmental Protection Agency.

McDonal, T.A., 2002. A perspective on the health risks of PBDEs. Chemosphere, 46, 745-755.

Nepali Times, 2004. Official wrangling and greed delay the cleanup of an obsolete stockpile of dangerous pesticides. 11-17 June.

Niessen, W.R., 1995. Combustion and Incineration Processes. ISBN 0-8247-9267-X. Marcel Dekker, Inc., New York.

Oberacker, D.A., 1988. Incineration options for disposal of waste pesticides. Pesticide waste disposal technology, Bridges, J.S and Dempsey, C.R (eds.), US

Environmental Protection Agency, Noyes Data Corporation, ISBN: 0-8155-1157-4.

Oberacker, D.A., 1989. Test burn for banned pesticides. *Journal of Hazardous Materials*, 22, 135-142.

Oberacker, D.A., Lin, P.C., Shaul, G.M., Ferguson, D.T., Engleman, V.S., Jackson, T.W., Chapman, J.S., Evans, J.D., Martrano, R.J. and Evey, L.L., 1992. Characterization of emissions formed from open burning of pesticide bags. *Pesticide Waste Management*, Bourke, J.B., Felsot, A.S., Gilding, T.J., Jensen, J.K and Seiber, J.N. (eds.), 202nd National Meeting of the American Chemical Society, New York, 25-30 August. ISBN: 0-8412-2480-3.

Pesticide Manual, 1997. A world compendium. British Crop Protection Council. ISBN 1 901396 11 8.

POP's Inventory, 2003. POP's inventory in the agriculture in the Republic of Moldova. www.rec.md/download/POP's/NIP-E.doc

Schimpf, W. A., 1990. Disposal of pesticides and chemical waste in a cement kiln in Malaysia. *Pesticide Disposal Conference*, Niamey, Niger, 21-26 January.

Schimpf, W. A., 1998. Disposal of obsolete pesticides in a cement kiln in Tanzania – Experience with the incineration of Dinitro-o-Cresol in a cement rotary cylindrical

kiln in a developing country. 5th International HCH and Pesticides Forum, Bilbao, 25-27 June.

Science in Africa, 2002. Stockpiles of obsolete pesticides in Africa higher than expected. <http://www.sciencein africa.co.za/2002/october/pests.htm>

Shih, C.C., Tobias, R.F., Clausen, J.F. and Johnson, R.J., 1975. Thermal degradation of Military standard pesticide formulations. TWR Systems, Inc.

Schumacher, M., Bocio, A., Agramunt, M.C., Domingo, J.L. and de Kok, H.A.M., 2002. PCDD/F and metal concentrations in soil and herbage samples collected in the vicinity of a cement plant. Chemosphere, 48, 209-217.

Stobiecki, S., Fuszara, E., Baron, L., Silowiecki, A., and Stobiecki, T., 2003. Disposal of Obsolete Pesticides as an alternative fuel in cement kiln. 7th International HCH and Pesticides Forum, Kiev, 5-7 June.

Stretz, L.A. and Vavruska, J.S., 1983. Controlled air incineration of PCP. Los Alamos National Laboratory, US Environmental Protection Agency IERL/CI Incineration research branch, US EPA Interagency Agreement AD-89-F-1-539-0.

Suderman, R.W. and Nisbet, M.A., 1992. Waste derived fuel as a supplementary energy source at the Woodstock Cement Plant. Environment Canada, Report EPS 3/UP/6.

UNECE, 1998. The Aarhus Protocol on Persistent Organic Pollutants. United Nations Economic Commission for Europe. http://www.unece.org/env/lrtap/POP's_h1.htm.

UNEP, 2001. The Stockholm Convention on Persistent Organic Pollutants. United Nations Environmental Programme. <http://www.chem.unep.ch/sc/default.htm>.

UNEP, 2004. Review of the Emerging, Innovative Technologies for the Destruction and Decontamination of POP's and the Identification of Promising Technologies for Use in Developing Countries. www.unep.org/stapgef.

Vallack, H.W., Bakker, D.J., Brandt, I., Brorstrom-Lunden, E., Brouwer, A., Bull, K.R., Gough, C., Guardans, R., Holoubek, I., Jansson, B., Koch, R., Kuylenstierna, J., Lecloux, A., Mackay, D., McCutcheon, P., Mocarelli, P., Taalman, R.D.F., 1998. Controlling persistent organic pollutants - what next? *Environmental Toxicology and Pharmacology* 6 (3), 143–175.

Viken, W. and Waage, P., 1983. Treatment of hazardous waste in cement kilns within a decentralised scheme: the Norwegian experience. *UNEP, Industry and environment*, 4.

WHO, 2002. The WHO recommended classification of pesticides by hazard and guidelines to classification. ISBN: 92 4 154564 X.

WHO, 2003. Health risks of persistent organic pollutants from long range transboundary air pollution. <http://www.euro.who.int>

Withmore, F.C., 1975. A study of pesticide disposal in a sewage sludge incinerator.
US Environmental Protection Agency, EPA/530/SW-116c.