Cement Kiln Destruction of Surplus Pesticides in Morocco
Feasibility Study, September 1991

Reported by

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Introduction

A team comprising personnel and consultants representing A.I.D./Washington, USAID/Rabat, and Gesellschaft für Technische Zusammenarbeit (GTZ) visited Morocco in September 1991, to determine the feasibility of cement kiln incineration of surplus pesticides in Morocco. Team findings on cement kilns and on pesticide stocks are presented in the attached reports. Team members were:

Richard Bolwerk, GTZ Consultant, Pollution control engineer
Torben Enkegaard, AID/W Consultant, Cement engineer
David Evans, AID/OFDA, AAAS Fellow (Environment)
Said Ghaout, DPVCTRF, Entomologist
Gudrun Huden, AID/OFDA, Environmental Officer
Joe Kitts, USAID/Rabat, Locust Control Project
Wolfgang Schimpf, GTZ Pesticide Service Project

Acknowledgments

This field study continues the excellent collaboration between the Agency for International Development (A.I.D.) and the Gesellschaft fur Technische Zusammenarbeit (GTZ) in the field of pesticide disposal. A.I.D.'s Office of U.S. Foreign Disaster Assistance (OFDA) is indebted to GTZ's Pesticide Service Project for making available the services of Dipl-Ing. Wolfgang Schimpf who took samples from the various sites; for arranging for the analysis; and for generously providing consultant services of Dipl-Ing. Richard Bolwerk.

We are grateful to the Fuller Company of Pennsylvania for making arrangements with F.L. Smidth of Denmark to release Torben Enkegaard to undertake this study; and to Joe Kitts and Eric Loken of USAID/Rabat for special care in planning and facilitating this field trip. We are particularly grateful to Said Ghaout for his insight and professionalism throughout this trip, enabling us to better understand the historical issues.

History

Accumulation of out-dated pesticides presents a problem in a number of countries. Very often these pesticides were acquired for grasshopper/locust control, with gradually-increasing stocks of toxic materials stored under less than optimal conditions for long periods of time. Some products are no longer recommended for insect control (e.g., the chlorinated hydrocarbon pesticides), and some of the material has degraded, the storage containers deteriorating to the point of leakage or spillage. Risk to human and environmental health is both acute and constant, and communities surrounding these pesticide stores are at especially great risk.

A large accumulation of pesticides has resulted from many years of locust control campaigns in Morocco. Two major pesticides in this accumulation are:

- BHC: (Chlorinated hydrocarbon, 1,800 tons)--formulated as liquid, powder and bran baits: outdated, and no longer used in control. The liquid is stored in badly-corroded drums; the powder and bran are in paper bags.

- Malathion: (Organophosphate, 300,000 liters)--formulated as ULV liquid. Analysis of the samples taken in September 1991 by GTZ at three sites surprisingly showed little, if any, deterioration. The label carries a 3-year date of expiry, but the drums are over three years old and stored under high-temperature conditions. (Note: American Cyanamid malathion drums have suffered unusual, early corrosion.)

Cement kiln incineration as a disposal technique

High temperature incineration is a useful technique for disposal of pesticides. Since combustion temperatures of pesticides range from about 400-900 °C, it is useful to seek out reliable incineration at considerably higher temperatures (cement kilns operate between 1200-2000 degrees C). Lower temperatures will result in incomplete destruction of pesticides and uncontrolled release of toxic emissions into the atmosphere. While burning the compounds in dedicated incinerators can be an effective means of disposal, the process is costly and appropriate "mobile" facilities need to be leased and imported, or constructed at a fixed site.

Cement kiln incineration has great promise in destruction of hazardous materials. Temperatures and residence times in cement kilns are greater than those of hazardous waste incinerators: the result is complete destruction of even very stable organic compounds after 2 seconds. Cement kilns have been used for hazardous waste disposal over the past 20 years in industrialized countries; successful surplus pesticide disposal operations have been conducted in Malaysia and Pakistan, and are in process in Nepal under UNDP sponsorship. The technique is advocated by Groupement International des Associations Nationales de Fabricants de Produits Agrochimiques (GIFAP) as an effective and inexpensive means of pesticide disposal.

Only slight modification of the kiln is required: liquid material is fired using conventional oil burners, and solids can be treated like coal dust.

Hazardous waste often has high fuel value, saving the cement manufacturer substantially by reducing primary fuel requirements. The procedure results in national self-reliance in dealing with surplus pesticides and may also be used to dispose of other hazardous wastes or "nuisance" materials, such as old tires.

AID/GTZ feasibility study in Morocco

The AID/GTZ team visited some of the major sites of pesticide stores including those of the Centre National de la Lutte Anti-acridienne at Ait Melloul, and those at Foum-El-Hissen, Taroudant and Tiznit. These and other stores have been variously described in reports by Messrs Krueger and Jackson, among others. The AID/GTZ team was more concerned with qualitative rather than quantitative field observations, at the end of which we agreed with the Government of Morocco that the problem of disposing of these useless commodities is of enormous dimension and great urgency.

Sampling and analysis: Samples of liquid and powder formulations (20 ml and 100 g) were taken at F. El Hissen, Taroudant and Tiznit, and soil samples (150 g) from surface and 30 cm depth of visibly contaminated soil at the Tiznit compound. The analysis was to determine percent of active ingredient, decomposition products, solvent in BHC liquid formulations and contamination products in the soil. GC/GC-MS were the analytical methods employed by the Formulation Control Laboratory, and Pesticide Residue Laboratory, of the GTZ.

Counter to expectations, the BHC liquid labeled as 10 or 15% active ingredient showed a potency three times higher (up to 51%); similarly, the powder formulations had an actual content three to four times higher than marked. Percentage of active ingredient for the 95 or 96% marked malathion ranged from 87-96

percent; the product is considered still in good condition and usable. The soil was found to be highly contaminated, mostly with BHC. (Note: Torben Enkegaard estimates that there may be 1000 cubic meters of contaminated soil in need of disposal). Details of the sample analysis are given in the attachment to this report.

The team visited two of Morocco's nine cement plants: "ASMAR" in Marrakech and "CIOR" in Oujda. The technical consensus of the team was that the ASMAR plant, while not ideal, could be adapted (without major changes to the plant) to handle all three types of pesticide wastes: liquid, solids, and contaminated soil. The Oujda cement kiln was ruled out as a site for pesticide disposal as it cannot deal with the large volume of the organochloride, BHC.

Attributes of cement plants required for pesticide disposal

In studying published specifications (Cembureau, World Cement Directory, 1991) of Moroccan cement plants, it appears likely that some provide better technical prerequisites than the plants observed by the team. These aspects, and potential candidate cement plants, are discussed in the accompanying reports.

The greatest concern to the cement maker is minimizing the amount of Cl in the kiln. Introduction of BHC would increase the Cl content, but measures can be taken to assure that the Cl is within levels of tolerance. One remedy is installation of a bypass for removal of Cl during the production process which -- as noted by the chief engineer at the ASMARA plant -- is necessary (and already planned) for optimal cement making conditions. Open kiln systems, such as Lepol kilns and long dry or wet kilns, are able to accept higher amounts of Cl. The attached reports also discuss prerequisites for introducing the two types of pesticides (OP's and OC's) and formulations at flow rates that do not endanger the efficiency of the cement making operation.

Prerequisites to a pesticide disposal operation

1) A pilot phase to obtain baseline and waste burning emissions samples, followed by analysis. Samples are also analyzed of raw materials and soil within a certain range and prevailing wind direction from plant ("emission maximum"). Use of facilities of the National Analytical Laboratory (Casablanca) should be made possible with a high priority attachment. Baseline tests will establish characteristics of the normal incineration process, so comparison can be made with later pesticide burn emissions. Baseline parameters to be established are:

Oxygen (O_2); Carbon dioxide (CO_2); Carbon monoxide (CO); total carbon (C); dust (mg/cubic meter); sulfur content; dioxifurans; products of incomplete combustion (PICs); dust content; temperature at raw material feed end; temperature of clinker as it leaves the kiln; degree of negative pressure in firing zone.

2) Determination of Ministry with chief responsibility for planning and execution of pilot and implementation phases. Authority and responsibilities must be resolved before any further steps can be taken. Possibilities would be Ministries of Interior or Agriculture, or the Gendarmerie Royale. The Ministry of Health, among others, must take an active role in assuring and monitoring safety. (Training could be provided by donors, if necessary).

3) Approval of Board of Directors of plant (if private), and/or cement makers trade association.

4) Institution of an effective public awareness program to inform cement plant employees, residents of nearby communities, and the press well in advance of implementation. Concern for safety of the human population and the environment is to be stressed, and spokespersons from the scientific and civic community should be involved in a public forum to air concerns and put them to rest.

Safety and environmental concerns

There is sufficient evidence to state categorically that stack emissions will not be more hazardous than during "normal" cement production operations. Emissions monitoring is a vital component of the pilot phase of any disposal activity. The project will align with two major sets of international emissions standards: USEPA (United States) and TA Luft (Germany). Emissions to be tested are: DRE, CO, HCl, SO_2, SO_4, PO_4. Consideration will be given to emissions monitoring location(s), the ability to obtain continuous checks on the firing process, and assurance that all monitoring probes are in satisfactory condition.

Safety during transport of pesticide stocks to the cement kiln disposal site will take a number of factors into account:

- Distance of stocks from the kiln.
- Quality of roads: Road surfaces in Morocco are generally good, but there are some difficult spots at access roads to depots. Steep winding grades over Atlas Mountains should be avoided when possible. Roads are relatively narrow, and traffic control by military escort with radio communication is needed.

- Timing: Transport is best done during the dry season to avoid water flow over roads--ideally in March or April, before the hot summer.

- Choke points: Transport routes should avoid city or village traffic if possible.

- See also logistics plan in Pakistan Pesticide Disposal Report, and Lessons Learned from the Niger Dieldrin Disposal Plan (May, 91; in press).

Measures to insure safety in handling pesticide stocks will include:

- Training of all personnel involved in pesticide handling or transport.

- Adequate protective gear and training in use.

- Assessment of the most appropriate methods for handling stocks with corroded drums in order to minimize handling and leaks: Either pumping into tanker/containers on already-contaminated depot site; or overpacking and removal to disposal site.

- Availability of medical personnel/assistance.

- Equipment and training for control of spills.

- Cleaning of empty drums; disposal of rinsate and drums.

- Provision for receiving, storing, blending and handling of waste products at kiln site.

Costs

Costs presented are for modifications at the site of pesticide disposal.

Other expenditures would be associated with preparation of logistics and site safety plan, handling and transporting of pesticides, protective gear, safety training, public and media relations. Most of these should not require much donor assistance.

Shredder, pipes, fan, blower, shutoff devices	$ 100,000
Firing gun, support	$ 20,000
Burner modifications, nozzle system for liquids (Pillard)	$ 10,000

Feed system: compressor, pumps, flow meter, dirt filter (liquids), valves, etc.	$ 50,000
Laboratory equipment, supplies	$ 20,000
Tanks, preparation, transfer station	$ 50,000 - 250,000
Construction of containing area, loading zone, lowering floor	$ 50,000
Protective surfacing	$ 50,000 - 80,000
TOTAL RANGE	$ 350,000 - 580,000

(Installation of a chloride bypass system would cost approximately $1,000,000 -- something the ASMAR plant plans to install in 1992 in any case, along with other improvements.)

Recommendations and Action Plan

Given comparative known costs of other disposal methods (among these shipment to Europe for disposal in a dedicated incinerator; or disposal via leased "mobile " incinerator estimated at $13/liter), the case for cement kiln incineration becomes very persuasive. While all efforts should be made to minimize pesticide and other wastes through better management, some need for disposal of obsolete products and industrial wastes will always exist. With a cement plant equipped to burn such hazardous material, the country would be independent of the repetitive need to look for capital intensive solutions from the outside. With this longer view in mind, it is suggested that the GOM consider the optimal plant choice.

The task, while complex, looks less formidable when one lists the individual steps in approximate chronologic order. Given the will, the project appears quite doable with minimal assistance from the outside. There are of course firms that specialize in waste processing as a turnkey operation, at a price.

a) Determine GOM commitment to a dedicated hazardous materials disposal system which would serve future needs.

b) Cost out other disposal options, both immediate and long-term.

c) Determine responsibilities: agency in charge.

d) Allow free access of consultants for inspection of other cement kilns to determine most suitable plant.

e) Decide on specific plant; obtain agreement from cement maker and diverse ministries and other authorities (in writing).

f) Provide for Moroccan cement engineer to visit cement plant burning hazardous waste in Europe, the U.S. or Canada.

g) Develop specifications for adaptations to kiln (consultant).

h) Prepare public information and awareness campaign (consultant in collaboration with Moroccan scientist/environmentalist).

i) Develop logistics plan.

j) Request bids for equipment and materials to be imported; place orders.

k) Develop site safety plan.

l) Begin training in pesticide handling, site safety, and spill control.

m) Receive (customs waived) equipment and install.

n) Construct handling and containment measures at kiln site.

o) Collect pesticide and truck to site for pilot operation.

p) Analyze sample of pesticide batch for pilot operation (Casablanca laboratory); establish flow rate.

q) Conduct baseline and pesticide burn tests: stack emissions, clinker and dust, also downwind soil collection.

r) Analyze samples and compare with U.S. and German standards for Destruction Removal Efficiency. Establish optimal flow rates for normal operations.

s) Begin major disposal operation around the clock.

t) Schedule and execute visit of Algerian, Tunisian, Egyptian, Pakistani cement makers to observe this technology under operating conditions.

u) Publish results of pilot operation and experience, including costs, of daily operations of the large-scale project.

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To
Mrs. Gudrun Huden,
Mr. David Evans
OFDA/PMP, Washington DC, USA

Ref. Analytical results

Dear Gudrun, Dear David

enclosed you find the analytical results of the pesticide and soil samples, colleted in Marocco during our study tour in September 91.

The conclusions of the anlytical results are:

1. BHC

1.1 The chlorine content in all the BHC-liquid and dust formulations are 3 times higer than expected. The BHC-formulations are technical products, which contain all the isomeres. The BHC is labeled as 10 and 15 % respectively, related to the gamma-isomere (see Annex I). This information should be taken in concideration by the calculation of the BHC-input into the cement kiln.

1.2 The sample 6/1 - 6/4 from the Tiznit-store could not be identified as BHC or Malathion. According to the analysis by GC/MS we presume that the sample materials are totaly decomposed thiophosporic ester.

1.3 According to the analyis by GC/MS, the solvent in the BHC-samples is a mixture of substitute benzene and naphthalene.

2. Malathion

2.1 The Malathion is still in good condition:
According to our experts, the pesticide could be used as ULV-formulation.

2.2 Differences in the actual content of active ingredience (a.i.) can results from the sampling technique and normal analytical errors.

3. Soil samples

3.1 The results of the soil samples from the Tiznit store confirm the visible impression, that the soil ist higly contaminated with BHC and Fenitrophion. Contarmination with Malathion has not been confirmed.

3.2 The soil sample (taken behind the house and the garden of the watch-man !!!) outside the Tiznit store is also contaminated with BHC: sample 10/2, Annex III.

Please inform Mr. Torben Enkegaard about these results.
The Bolwerk-report is still in process.

With best regards

W.A. Schimpf

Dr. G. Vaagt

Encl.

cc: Joe Kitts/Locust Control Coordinator, US-AID/Rabat

Analytical Results of the BHC from Marocco:

Sample No.	Location	Formulation	Declared Content	Actual Content	Method
1/1	Fam El Hisn	Liquid	15 %	43 % total BHC	GC
1/2	"	"	15 %	43.7 % "	GC
1/3	"	"	15 %	46.3 % "	GC
1/4	"	"	15 %	47.5 % "	GC
1/5	"	"	15 %	51.8 % "	GC
3/1	Taroudant	Liquid	15 %	50.5 % "	GC
3/2	"	"	15 %	47.6 % "	GC
3/3	"	"	15 %	49,7 % "	GC
3/4	"	"	15 %	44.4 % "	GC
3/5	"	"	15 %	49.7 % "	GC
5/1	Taroudant	Dust	3 %	8.3 % "	GC
5/2	"	"	3 %	8.8 % "	GC
5/3	"	"	3 %	9.7 % "	GC
5/4	"	"	3 %	8.6 % "	GC
5/5	"	"	3 %	8.2 % "	GC
8/1	Tiznit	"	3 %	9.7 % "	GC
8/2	"	"	3 %	11.9 % "	GC
8/3	"	"	3 %	12.6 % "	GC
8/4	"	"	3 %	11.8 % "	GC

Analytical Results of the Malathion from Marocco:

Sample No.	Location	Formulation	Producer	Declared Content	Actual Content	Method
2/1	Fam El Hisn	Liquid	Am. Cyanamid	96 %	87.5 %	GC
2/2	"	"	"	96 %	90.0 %	GC
2/3	"	"	"	96 %	90.7 %	GC
2/4	"	"	"	96 %	89.8 %	GC
2/5	"	"	"	96 %	91.1 %	GC
4/1	Taroudant	Liquid	Cheminova Agro	95 %	93.1 %	GC
4/2	"	"	"	95 %	91.6 %	GC
4/3	"	"	"	95 %	88.6 %	GC
4/4	"	"	"	95 %	87.5 %	GC
4/5	"	"	"	95 %	93.8 %	GC
7/1	Tiznit	Liquid	Am. Cyanamid	96 %	93.4 %	GC
7/2	"	"	Cheminova Agro	95 %	90.1 %	GC
7/3	"	"	Am. Cyanamid	96 %	96.2 %	GC
7/4	"	"	Cheminova Agro	95 %	94.7 %	GC

Analytical results of the soil-analysis in Tiznit-store

Sample No	Location	Results* total-BHC	Fenitrothion
9/1	Black spot (surface)	20.46 %	-
9/2	Black spot (30 cm deep)	6.23 %	-
9/3	Brown spot (surface)	124 ppm	1.4 %
9/4	Brown spot (30 cm deep)	20 ppm	0.05
10/1	Surface soil (on the fence, opposite the gate) -> baseline within the compound	709 ppm	-
10/2	Surface soil (outsite the pesticide store) -> baseline outside	22 ppm	-

* Analysis of Malathion is negativ

Remark:

BHC-Isomers

All BHC isomers are still in the product. The consequence is, that the chlorine concentration is about 3 times higher than expected. The average of the isomere-distribution in the analysed BHC is :

Alfa-BHC:	15 %
Beta-BHC:	7 %
Gamma-BHC:	27 %
Delta-BHC:	42 %
Etha-BHC:	9 %
Total:	100 %

All the isomers are present in technical BHC in considerable quantities and result from the chlorination of benzene. Theoretically BHC can exist as 17 optical or stereo isomers. However spatial and energy systems considerantions show that only 9 of these isomers are possible.

Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH

Pesticide disposal at the ASMARA cement works in Morocco

by

Dipl.-Ing. Richard Bolwerk

Feasibility study commissioned by the
Deutsche Gesellschaft für
Technische Zusammenarbeit (GTZ) GmbH
6236 Eschborn, Federal Republic of Germany

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Abstract:

Within the scope of a pilot project on "Pesticide disposal" implemented by the Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH, a study is to be conducted, in support of a US Foreign Disaster Assistance project, to establish whether the large quantities of old pesticides stored in Morocco can be burned on the spot in a rotary cement kiln in Morocco.

Essential prerequisites for environmentally sound pesticide disposal are problem-free continuous operation of the installation, even feeding of the substances via the kiln's primary end and a safety system which ensures that burning takes place only when specific operating parameters (e.g. temperature, quantity of raw meal, primary fuel) are observed.

In addition, appropriate measures must ensure that the increased chlorine input does not give rise to operational problems in the calcining and transitional zone (kiln-preheater zone). Depending on the plant's nature and mode of operation, this calls for controlled raw-material and fuel feed in addition to special process technology.

These prerequisites, together with constant high-temperature conditions accompanied by long gas sojourn times in the high-temperature zone, a material composition giving a highly basic reaction and an oxidising atmosphere, permit high destruction efficiency coupled with emissions remaining within existing ranges of variation.

1.0 Terms of reference

A study is to be conducted to examine the possibility of disposing of old pesticides in rotary kilns operated by the cement industry in Morocco.

The study is to describe the technical measures necessary to ensure correct, problem-free burning.

It is to state whether pesticides can be disposed of in this way without giving rise to additional environmental pollution.

1.1 Cement works in Morocco

Two cement works were visited in the course of a stay in Morocco in September 1991 in connection with the GTZ pilot project "Pesticide disposal":

1. ASMARA cement works, Marrakesh
2. Oujda cement works

Both plants comprise high-temperature burning installations in the form of a rotary kiln with preheater. They therefore guarantee that by virtue of the

- gas temperatures of 1200 - 2000° C
- clinker burning temperature of 1350 - 1400° C
- gas sojourn times in the kiln of more than 2 seconds
- oxidising atmosphere and the
- highly basic composition of the combustible

the destruction efficiency of at least 99.99 % required for burning pesticides is achieved.

2.0 Oujda cement works

The Oujda cement works operates two parallel rotary kilns, each 72 m in length and 4.6 m in diameter, with cyclone preheater and satellite cooler. The plant has a capacity of 2 x 1800 tonnes/day. The existing

oil lance is used to start up the kiln; the kiln is otherwise fired using coal dust. The raw materials, clay and limestone, are prepared and fed to the kiln at this plant too in the manner described in Section 3.1 below. The oxygen content (O_2) downstream of the preheater is approx. 5 %. The dust content of the exhaust gases is roughly 100 mg/m^3 (data supplied by operator).

The burner system currently installed in Oujda does not permit optimum kiln operation. The specific operating conditions with regard to flame regulation lead to changes in the temperature curve with the result that some of the chloride condenses in the kiln, leading to formation of rings and deposits.

Experience indicates that installation of a bypass to draw off a partial gas flow of around 5 - 10 % from the kiln feed end at the Oujda plant could remove some 10 - 30 % of the chloride from the kiln. Such a measure would make it possible to remove from the kiln system precisely that quantity of Cl which cannot be removed with the clinker or the dust and consequently leads to enrichment. In line with current standards, the bypass gases would then be routed to special installations in which the kiln gas can be quickly cooled from a temperature of 1000 - 1200° C to 300 - 400° C and the dust removed from it by means of a special filter.

When considering the installation of a new bypass system, careful attention should also be given to establishing how the raw-material and heat potential of the bypass flows could be incorporated into the overall manufacturing process at the cement works. Depending on its design and extent, a corresponding overall system would cost around $ 2,000,000.

Input of chlorine from the pesticide BHC can give rise to increased enrichment of alkali halides in the calcining and transitional zone, accompanied by ring formation.

Reduction of the burden on the internal cycle at the ASMARA cement works therefore plays an important role in the decision as to which of the plants could be used to burn pesticides. As stated above, no such facility exists at the Oujda cement works. The Oujda works could be equipped for burning pesticides by changing the raw materials and fuel and by installing a bypass; however, this would necessitate more extensive measures than in the case of the ASMARA cement works. Moreover, the ASMARA plant is also to be preferred on account of the fact that it is closer to the pesticide stores.

My comments will therefore be confined to the requirements at the ASMARA plant, as only minor modifications to the tried and tested technology are required here.

3. ASMARA cement works

3.1 Description of process

The ASMARA cement works (Marrakesh, Morocco) operates a rotary cement kiln with cyclone preheater and grate-type clinker cooler. The kiln is 64 m long and has a diameter of 4.4 m. It is fired with coal dust.

The raw materials, clay and limestone, are blended in accordance with the quality requirements for the end product, crushed and ground in ball mills. The mills are heated by means of a partial flow from the kiln exhaust gases, utilising the quantities of heat contained in the gases.

The raw meal produced is stored in silos and is then burned.

The raw meal is fed continuously to the kiln by means of mechanical conveyors. After being preheated in stages in a cyclone preheater, the material heated to approx. 900° C by the kiln exhaust gas in counterflow enters the rotary kiln and is burned there at a temperature of around
1450° C to produce clinker. The hot clinker is then air-cooled in a cooler and is subsequently routed via a silo to the cement mills for grinding.

Some of the hot exhaust air produced during clinker cooling is routed into the rotary kiln as secondary air.

The hot exhaust gas leaving the rotary kiln heats the raw meal in counterflow in the preheater. The dust collected in the electrostatic precipitator is returned to the raw meal.

The rotary kiln is fired at the primary end at the burner tip using coal dust. No substances are introduced into the kiln at the secondary end.

3.2 Description of burner

The rotary kiln's main burner is installed in the middle of the kiln centre-line. It takes the form of a so-called three-duct burner made by the Pillard company, with a separate oil lance located coaxially below the burner axis.

The coal-dust burner has a central guide pipe for feeding the coal dust/air mixture (first duct). This burner pipe is surrounded by a jacket to guide the swirl air (second duct) and a further jacket for the axial air supply (third duct).

The axial air and swirl air are introduced via a common flexible supply hose; the air quantities can be adjusted separately within specific limits. A partial flow of primary air for the oil lance is drawn off from the axial air supply line.

The oil burner has a feed pipe and a return pipe and is surrounded by the nozzle-connection guide tube which, along with the nozzle holder, serves to introduce the primary air.

According to the operator, the oil lance is at present used only to heat the rotary kiln upon start-up. The regulating devices for the oil feed are located on the kiln control panel. The oil feed and oil return flow are shut off by means of manually operated valves. The feed line also contains a solenoid valve and the consumption meter. The oil lance additionally incorporates a blow-out device which uses compressed air to blow the remaining oil out of the lance when the oil

feed is switched off once the kiln has heated up. This is necessary in order to prevent coking of the burner nozzle caused by the oil in the line.

3.3 Mode of operation of the kiln

The rotary cement kiln is started up using fuel oil, which is fed to the kiln via the oil burner described above. Once the kiln temperature has reached approx. 600° C, the coal-dust burner is put into operation to further heat the kiln. Once the coal-dust burner has been ignited, the oil feed is maintained until 70 % nominal raw-meal throughput is achieved. The raw-meal feed is effected via the suspension preheater when the exhaust-gas temperature at the kiln feed end reaches approx. 1100° C.

When the rotary kiln is in continuous operation, coal dust is used as the principal fuel.

In normal operation, the clinker output is 1400 tonnes/day.

3.4 Characteristics of continuous operation and continuous monitoring

Problem-free continuous operation is characterised by a raw-meal feed of approx. 95 tonnes/h and a fuel throughput of approx. 7 tonnes of coal/h. According to the operator, the dust content of the exhaust gases downstream of the electrostatic precipitator is 100 mg/m^3 (standard condition dry). At 100 % nominal raw-meal throughput there is - in accordance with the design - a gas exit temperature of approx. 1100° C and a raw-meal feed temperature of approx. 800° C at the kiln feed end; at
the kiln discharge end (burner) the gas inlet temperature is 850° C and the material exit temperature is 1350 - 1400° C. These data may vary somewhat depending on the degree to which the capacity of the rotary kiln is utilised. Experience to date indicates that the oxygen content should be 5 - 7 % by volume.

The kiln at the cement works offers the following possibilities for checking and continuously monitoring these operating conditions:

1. Fuel throughput measurement, measuring point between coal feeder and burner

2. Raw-meal throughput measurement downstream of raw-meal silos

3. Gas exit temperature measurement at kiln feed end (measuring point should be in riser between rotary kiln and suspension preheater)

4. Material exit temperature measurement at kiln discharge end (measuring point directly at kiln discharge end before material enters clinker cooler)

5. O_2 measurement between fan and conditioning tower

6. Carbon monoxide measurement upstream of electrostatic precipitator

7. Measurement of dust concentration in exhaust gas, measuring point downstream of electrostatic filter in exhaust gas stack

The temperature measurements performed at the kiln's feed and discharge ends play an important role in monitoring a problem-free burning process.

The data recorded at the other measuring points, such as CO measurement, raw-meal throughput, fuel throughput, dust concentration in exhaust gas and O_2 content, are necessary for ensuring that the desired operating conditions are maintained.

3.5 Operating problems: description, characteristic features and measures

Normal kiln operation may be disrupted by operating problems in the course of the period of operation. These may be of a mechanical or electrical nature, or may relate to aspects of the process, e.g.:

- Mechanical problems, e.g. material fracture, consequences of wear

- Disruption of raw-meal feed, e.g. blockages in the conveying equipment or in the cyclones

- Disruption of fuel feed
- Deviation of temperature from desired value
- Increased CO formation in exhaust gas
- Power failures

Appropriate steps and reactions are laid down for the operating personnel in the event of such problems; these must be extended for the input of the supplementary materials.

In the event of increased CO formation in the kiln exhaust gases, the electrostatic precipitator system is automatically switched off as soon as the set CO threshold is reached. An early warning should be given in good time when a CO level of approx. 0.3 % by volume in the exhaust gases is reached so that the operating personnel have the opportunity to take prompt countermeasures, e.g. reducing the fuel feed or correcting the combustion setting, in order to prevent unnecessary shutdown of the kiln installation.

Power failures mean that the combustion-air blowers, electrostatic precipitator, material conveyors, drive system etc. will cease to operate. This immediately stops the fuel feed and the exhaust gases still in the system are removed by means of the stack's natural draught.

4.0 Proposals regarding input of pesticides and description of accompanying measures

On the basis of the investigations conducted in Morocco and the assessments made, and in conjunction with the experience gained in this field regarding the input of secondary substances in rotary kilns operated by the cement industry, the measures outlined in Sections 4.1 to 4.6 below are proposed with a view to ensuring problem-free pesticide disposal:

4.1 Requirements to be met by the feed system

A burner or feed lance independent of the main fuel, together with appropriate regulating and supply systems, is essential for operating the cement kiln with the pesticides mentioned.

The central feed duct for Malathion and shredder-processed BHC, located in the burner or feed lance, is to be fitted with valves which ensure that proportioning is reliably and rapidly stopped if there is a power failure or if the safety chain responds. For fast shutoffs of this nature it is also necessary to have a device which will blow out (e.g. using compressed air) the remaining volume into the combustion chamber. It should be aimed to minimise the volume of the proportioning chamber to be blown out. In my opinion, the proportioned quantity should additionally be ascertained and recorded with the aid of a calibrated volumetric flow meter (display in control room). The quantity of pesticide must be limited to the maximum determined in the course of the test.

4.2 "Safety chain" to ensure problem-free continuous operation

Provision must be made for automatic shutoff of the substance feed by means of an upstream safety chain if the required burning conditions are not fulfilled, e.g. if the installation is not operating at an adequate level of capacity utilisation. This safety chain must act directly on the quick-acting valves in the feed line. It must be ensured that pesticide feed is possible only after the required operating conditions have been achieved.

The safety system must be designed such that the quick-acting valves are operated if one of the following chain elements responds:

1. Gas temperature at kiln feed end drops below 800° C

2. Temperature of combustible at kiln discharge end drops below 1250° C

3. A specific CO content (% by volume) - to be determined in the course of the test - is exceeded

4. Impermissible deviations are found in the comparison of desired/actual values at the coal-weighing machine

5. Raw-meal feed quantity drops below 75 % of maximum possible quantity

6. The vacuum - to be determined in the course of the test - upstream of the exhaust-gas fan drops below the required value

7. Failure of electrostatic precipitator

8. Failure of exhaust-gas fan

9. Failure of burner

Minor deviations from the above values are possible.

In order to permit precise determination of the threshold values in the safety chain, the temperature sensors at the kiln feed and discharge ends must first be calibrated, with the nominal load being varied; the representative nature of the measuring points must also be assessed. The load range within which the burning of pesticides is acceptable can then be determined on the basis of the results. The necessary threshold values for the monitored temperatures are obtained at the same time.

4.3 Problem-free feed via the primary end of the rotary kiln

The liquids (BHC and Malathion), solids (BHC powder) and contaminated soils to be disposed of must be fed evenly into the kiln via the primary end (burner end) in order to bring them together with the kiln's flame front by means of appropriate turbulence.

4.3.1 Liquids (BHC and Malathion)

If liquid pesticides are to be burned with as few problems as possible, the individual containers must be largely homogenised. This means that the batches must be mixed in order to balance out the

concentration. Mixing can take place either in a stationary tank using a suitable agitator or in a tank truck.

Depending on the design data, a filtration device which retains particles larger than 1 mm must be installed directly before the point where the substance is injected into the cement kiln's combustion chamber - in accordance with the burner manufacturer's directions - in order to ensure that the pesticides can be burned without problems. The pesticides can be fed in via the existing oil lance, as this is used only for starting up the kiln. However, the existing nozzle connection cannot be used and must therefore be replaced.

4.3.2 Solids (BHC powder)

Here again, problem-free burning is possible only if the containers are pulverised to a large extent (shredder) so that the packaging together with the BHC powder forms a homogeneous substance capable of being air-borne. A separate lance is required for injecting the substance into the primary end of the kiln. The solid and pulverized components should be injected via the lance into the cement kiln's combustion chamber directly from the shredder by means of a blower. If possible, the lance should be located above the main burner.

The lance's nozzle diameter should be matched to the size of the shredded material. In order to ensure that it does not become clogged, it should not be too small.

The pulverised material can be drawn from the shredder using manually-operated stop valves and an adjustable proportioning device.

A suitable shredder could be installed on the kiln platform near the opening so that the individual batches can be fed to the shredder by means of a crane.

4.3.3 Contaminated soils

The soils contaminated with Malathion and BHC should also be disposed of in the rotary kiln.

Fine-grained, sandy fractions should be fed to the kiln's primary end via the lance for pulverised material from the shredder. The remaining coarse components could then be routed into the kiln via the secondary end by means of a feed hopper.

4.4 Test steps for determining the input quantities

The pesticides mean that additional quantities of chlorine enter the kiln system. As a result, there is a possibility that the formation of deposits and rings in the lower part of the preheater will additionally disrupt kiln operation.

The chloride bypass must therefore be kept in continuous operation such that the total quantity fed to the kiln does not exceed approx. 0.2 g Cl/kg of clinker.

As the origin of the element concentration - whether it be the raw meal, the coal or the pesticide - has no major influence on the cycle behaviour of a kiln installation, the chlorine load to be introduced via the pesticide can be reasonably high in cases where the available raw materials and fuels have a low chlorine content.

The optimum possible pesticide quantity - particularly in the light of the raw materials and fuels - must therefore be determined in a multi-stage test. It is recommended to employ the three phases set out in the Table below, for liquid and solid pesticides in each case:

Test	Liquids (BHC and Malathion)	Solids (BHC powder)
1	3 l/min.	3 kg/min.
2	6 l/min.	6 kg/min.
3	10 l/min.	10 kg/min.

4.5 Trial operation and emission measurements

Before pesticides are fed to the kiln, the reliability of the safety chain must be tested by simulating faults. The emission data for the

cement kiln in normal operation should first be recorded by way of a zero-point measurement.

The following parameters should then be continuously monitored and recorded during the trial phase and when the substances are introduced:

- Oxygen (O_2)
- Carbon monoxide (CO)
- Carbon dioxide (CO_2)
- Total organically bound carbon (total C)
- Dust
- Temperature of clinker at kiln discharge end
- Temperature of kiln gas at kiln feed end
- Vacuum upstream of exhaust-gas fan

The following substances should be recorded by means of at least three individual measurements in the course of reference measurement and the trial phase:

- Sulphur dioxide (SO_2)
- Nitrogen oxides (NO_x)
- Gaseous inorganic chlorine compounds, given as hydrogen chloride (HCl)
- Inorganic gaseous chlorine compounds, given as (Cl^-)
- Polychlorinated dibenzodioxins (PCDD)
- Polychlorinated dibenzofurans (PCDF)

For the purpose of documenting pollutant enrichment, clinker and precipitator dusts should be removed from the process at same the time the emission measurements are made and the organic compounds analysed in one sample from the test series in each case. It is also recommended that coal dust, kiln meal and clinker dust be removed and retained as stock samples in order to provide additional information.

Soil samples should also be taken in the direction generally followed by the wind coming from the plant - in my opinion this should be done on the opposite side of the road near the olive trees and possibly also in the vicinity of the residential area - so that they may be examined for PCDD and PCDF. Attention should be paid to the maximum immission (pollutant deposition).

4.6 Safety during transportation, storage and transfer

The pesticides to be destroyed can be transported to the cement works in tank trucks or dry-bulk transporters.

It must be ensured at the cement works that any solids or liquids which may be discharged cannot penetrate the subsoil.

The unloading zone should therefore be designed as a containing area; it should be tightly sealed and resistant to the substances to be contained.

Collecting areas for spilled substances can be created by appropriately lowering the floor or installing raised sills.

There must be no drains within the loading zone.

The containing area should be made of concrete. It would then be resistant to a whole series of media over a certain period of time.

Safety can be further enhanced by means of appropriate surfacing, i.e.

- plastic sheeting with a special finish to provide surface protection or

- stainless steel sheet lining.

5.0 Summary

The burning of pesticides calls for a number of process-related measures in particular.

Relevant literature states that a temperature of 800° C and a sojourn time of 1.7 s are required for largely complete combustion of lindane.

With regard to the destruction efficiency for Malathion, a fire made it possible to establish that only 2 % of Malathion escapes undecomposed at combustion temperatures up to 600° C.

When organic compounds such as pesticides are burned, complete oxidation is likely, depending on the excess oxygen, the combustion temperature and the sojourn time of the combustion gases at high temperatures.

The main products of (complete) combustion are CO_2 and H_2O (in the presence of halogens, sulphur plus the corresponding haloid acids, sulphur oxides/sulphuric acids and phosphoric acid).

Substances such as HCl, sulphur oxides, nitrogen oxides and phosphoric acid are products of complete combustion given the presence of Cl, N, S and P in the active component, irrespective of the nature of the compound.

The bound sulphur contained in pesticides is converted into its oxides SO_2 and SO_3.

An emission forecast can be based on the reactions of the elements in question with other constituents of the combustible and of the kiln gas during the burning process.

Essential prerequisites for low emissions of gaseous compounds (S, Cl, P) are a composition of feed material, combustible and kiln dusts giving a highly basic reaction, (something which is always found in the clinker burning process), an oxidising composition of the kiln gas phase and the profile of the temperature curve.

This rotary kiln achieves gas temperatures of up to 2000° C; the kiln exhaust gases are exposed to temperatures in excess of 1200° C for at least two seconds. With a minimum expected destruction efficiency of 99.99 %, pilot tests and subsequent burning do not appear likely to give rise to any major problems.

As far as reliable burning of the substances is concerned, the rotary cement kiln has advantages over other burning methods.

Maintaining of a constant and very high temperature in the combustion chamber guarantees constant destruction efficiency.

The main firing system is not subject to any fluctuations caused by factors such as unexpected changes in the calorific value of the fuel or changes in plant load. The operation of a rotary cement kiln is characterised by a high degree of constancy in the region of the rated capacity, as process-related reasons mean that product quality assurance does not permit any changes in the temperatures or sojourn times in the kiln.

As pesticide disposal in rotary cement kilns is carried out solely by thermal means, malfunctions affecting the flue-gas dust collectors normally required have no effect on emissions of these substances.

In the course of operation as envisaged here, the emissions usually generated by rotary cement kilns will not change to any perceptible degree within the scope of the normal ranges of variation.

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Annex 1

Emission limits in Germany

	TA-Luft[1]	17. BImSchV[2]	
		Daily mean	Half-hourly mean
Dust	50 mg/m^3	10 mg/m^3	30 mg/m^3
HCl	30 mg/m^3	10 mg/m^3	60 mg/m^3
SO_2	0.40 g/m^3	50 mg/m^3	0.20 g/m^3
PCDD/PCDF	-	0.1 ng/m^3	
Total C	-	10 mg/m^3	20 mg/m^3
Min. temperatures	1200° C	1200° C	
Min. O_2 content	6 % by vol.	6 % by vol.	
Min. sojourn time	-	2 secs.	

1) TA-Luft = Technische Anleitung zur Reinhaltung der Luft (Technical Rules for Air Pollution Prevention), dated 27 February 1986 (rules for preventing harmful effects on the environment).

2) 17. BImSchV = 17th Federal Immission Control Ordinance - Ordinance concerning incinerators for wastes and similar combustible materials (November 1990).

Annex 2

Structural measures and facilities required	Cost
- Shredder, pipes, fan, blower, shutoff devices	$ 100,000
- Feed lance with support	$ 20,000
- Burner modifications, nozzle system for liquids (Pillard)	$ 10,000
- Feed system: compressor, pumps, flow meter, dirt filter (if liquids are used), valves etc.	$ 50,000
- Tanks, preparation, transfer station	$ 50,000 - 250,000
- Creation of containing area, loading zone, lowering of floor	$ 50,000
- Special surfacing to provide additional protection	$ 50,000 - 80,000

POSSIBILITIES OF INCINERATION OF PESTICIDES IN CEMENT KILNS IN MOROCCO

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SCOPE OF WORK

The Office of US Foreign Disaster Assistance (OFDA), of the Agency for International Development (A.I.D.), commissioned Fuller International, Inc., Bethlehem, PA, to provide services of a cement plant expert to a multi-disciplinary team to assist the Government of Morocco (GOM) in evaluating possibilities of incinerating overaged and surplus pesticides in cement kilns in Morocco.

ABSTRACT

The writer, who is employed by F.L. Smidth & Co. A/S, Copenhagen, Denmark (the parent company of Fuller International), spent the 11th to 19th, 1991, of September in Morocco visiting a pesticide storage facility at Tiznit and two cement plants, located at Marrakech and Oujda.

It can be generally stated that all cement kilns are ideally suited for destruction of non-chlorinated hazardous waste, including non-chlorinated pesticides. However, one of the two cement plants visited was struggling with chloride levels from raw materials which made it impossible to add further chloride to the system without costly modification to the plant.

The other cement plant was also receiving a considerable chloride input from the raw materials, but chloride was removed by a so-called bypass. It can be calculated that about 11 tons per day of bypass dust containing about 15% of salts is emitted into the atmosphere and that the salt emission will increase by about 15 - 30% if chlorinated pesticides are incinerated in the kiln as it presently operates. Other cement plants in Morocco operating more open kiln systems may actually be better suited for chlorinated pesticide disposal.

INCINERATION OF HAZARDOUS WASTE IN CEMENT KILNS

Hazardous waste incineration is an engineered process that employs thermal oxidation at high temperature (normally 900°C or greater) to destroy the organic fraction of waste. Any waste

with a hazardous organic fraction is at least a functional candidate for incineration; for example, significant amounts of contaminated water are currently incinerated in the United States, as are contaminated soils.

Minimum temperatures required for incineration range from 875°C for incineration of municipal garbage to 1400°C for incineration of more stable organic compounds such as PCB, dioxin, DDT, and residues from polyvinyl halogenide production. Residence time at the high temperature must be at least 2 seconds.

Producing cement clinker in cement kilns also involves high temperature burning. Liquid waste can be introduced into cement kilns using conventional oil burners; solid waste in the form of powder can be fired like coal dust.

Burning of liquid organic hazardous waste allows for recovery of substantial amounts of energy from waste materials. Cement production is an energy intensive process, and energy costs generally account for 33 to 40% of the cost of producing clinker. Waste fuels typically have a heat content comparable to coal or even fuel oil. By injecting liquid organic waste into the kiln as a supplemental fuel, cement kilns may greatly reduce use of primary fuels, thus providing substantial savings to the manufacturer. A cement kiln operator may actually be willing to pay for use of contaminated oil as fuel, for example.

In comparison with other types of hazardous waste incinerators, cement kilns possess several characteristics which make them an efficient technology for destroying highly toxic and stable organic wastes:

- Combustion gas temperatures and residence times in cement kilns exceed those of commercial hazardous waste incinerators. These high combustion temperatures and long residence times, along with the strong turbulence encountered in cement kilns, assure the complete destruction of even the most stable organic compounds. Burning of cement clinker requires a material temperature of 1400 - 1500°C, consequently the flame temperature must be even higher in order to obtain heat transmission from flame to material. In the case of short kilns like preheater kilns and precalciner kilns the gas temperature in the burning zone is about 2000°C, at mid-kiln it is about 1700°C, and at the kiln exit it is about 1100°C (ENCL. 1 & 2). The gas retention time is about 8 seconds.

- The large size of kilns and the quantity of heated material present, results in high thermal stability. In other words, temperatures within kilns change very slowly. Thus, even if a cement kiln is forced into an emergency shut-down resulting from a loss of primary fuel or a severe

malfunction, all hazardous waste in the kiln will be completely destroyed, provided automatic cutoffs prevent further injection of wastes.

- Cement kilns operate under alkaline conditions. Therefore, virtually all chlorine entering a kiln is neutralized fo form sodium chloride, potassium chloride, and calcium chloride, all relatively non-toxic substances. Consequently, emissions of hydrogen chloride, a strongly acidic compound, are significantly lower than emissions from commercial hazardous waste incinerators.

- Bottom ash resulting from incineration is incorporated into the clinker product, eliminating bottom ash disposal problems. Any metals contained in bottom ash are incorporated in the cement product as inert material. Cement quality is relatively unaffected by the addition of most impurities found in hazardous wastes and waste oil.

The present status of hazardous waste incineration in cement kilns is burning of primarily liquid waste in the firing end of the kiln. Most kilns burning liquid waste are wet process kilns, at least in the United States. One reason for this is that wet kilns are particularly fuel inefficient, and operators have been strongly motivated to reduce fuel costs. Another reason is that wet kilns can accept high inputs of chloride without expensive modification (up to 8 kg chloride per ton of clinker), whereas dry process kilns with 4-stage preheaters are limited to chloride inputs of 0.15 kg/t clinker (precalciner kilns) to 0.23 kg/t clinker (preheater kilns). If chloride input exceeds these figures, kilns must be equipped with costly bypass installations which, in the most extreme cases (precalciner kiln with 100% bypass for kiln tube gas) will allow total chloride input of 8 kg/t clinker. Chloride (present as alkali chlorides) needs in any case to be removed from the kiln system as precipitator dust, either from the main filter (wet, semi-wet and long dry kilns) or from the bypass filter (preheater/precalciner kilns).

Kiln tube exit gas temperatures are about 1100°C, which drops to 820°C (preheater kilns) or 900°C (precalciner kilns) a few tenths of a second after the gas leaves the kiln tube (ENCL. 1 & 2) when raw materials are introduced into the stream of kiln gas. Gas diverted through the bypass is quenched with cold air to even lower temperatures. Introduction of chlorinated wastes into the back end of preheater kilns or firing of these wastes into a precalciner are not recommended, as a temperature of at least 1200°C at 2 seconds retention time is necessary. Non-chlorinated solvents (turpentine, xylenol, etc.) may be burned in precalciners or introduced into the back end of preheater kilns without problems, and non-chlorinated solid waste may be treated in the same way: automobile tires are commonly introduced into the back end of preheater kilns where they burn without problems.

While it is common belief that chlorinated compounds such as PCB and dioxin, and such stable chlorinated pesticides as DDT are particularly resistant to incineration, such is not the case. The carbon-containing compound which is most difficult to destroy completely is carbon monoxide--which is generated in large amounts as the first combustion product of the fuel in all industrial combustion processes. Another carbon compound which is difficult to burn is methane, the main component of natural gas (ENCL. 3 & 4).

PESTICIDE STOCKS IN MOROCCO

The main problem from a disposal point of view is a comparatively large stock of hexachlorocyclohexane, $C_6H_6Cl_6$, abbreviated HCH. The compound is also known as benzene hexachloride or BHC (in the USA). The Cl content of BHC is 73.2%.

BHC stored in Morocco is the crude product, a mixture of various isomers. Only the gamma isomer, which constitutes 27% of the crude product, has insecticidal value. The material is 25-30 years old, and its use as an insecticide is prohibited today. Morocco stocks are in the following formulations:

10% gamma (37% total) in heavy aromatic naphtha	271,200 l.
15% gamma (55% total) in heavy aromatic naphtha	491,400 l.
Powder, 3% gamma (11% total) in talc	460,700 kg.
0.05% gamma (0.19% total) mixed with wheat bran	632,930 kg.

Total amount of pure BHC is calculated as 562,000 kg., corresponding to 411,000 kg. of Cl. The Specific Gravity of BHC is 1.85 g/cm^3, and that of the solvent is assumed to be 0.9 g/cm^3.

The energy value of the entire stock is nearly 7,000,000 Mcal (ton-calories), the equivalent of 1000-1200 tons of coal with energy values ranging between 6000 and 7000 Mcal/ton. While the BHC in talc has little heat value, the formulation adds magnesium to the system (talc is a magnesium silicate: $3MgO$, $4SiO_2$, H_2O). The MgO:Cl ratio in the 11% formulation is about 4:1, which means that addition of 0.1% Cl on a clinker basis is equivalent to 0.4% MgO, or 1.25% of the powder. The level must be considered when adjusting the chemistry of the raw mix fed to the kiln.

In addition to the BHC there is an accumulation of about 3,000,000 l. of other pesticides which have not been banned from general use, but which may have been rendered useless by storage in the open and in full sun for 2-3 years:

DDVP (Dichlorvos) $C_4H_7Cl_2O_4P$ M=221 d=1.42 g/cm^3

%Cl = 35.5 * 2 * 100 : 221 = 32.1%
%P = 31 * 100 : 221 = 14.0%, as P_2O_5 = 32.1%

Fenitrothion $C_9H_{12}NO_5PS$ M=277.2 d=1.32 g/cm^3

%P = 31 * 100 : 277.2 = 11.2%, as P_2O_5 = 25.6%
%S = 32 * 100 : 277.2 = 11.5%, as SO_3 = 28.9%

Malathion $C_{10}H_{19}O_6PS_4$ M=330.4 d=1.23 g/cm^3

%P = 31 * 100 : 330.4 = 9.4%, as P_2O_5 = 21.5%
%S = 2 * 32 * 100 : 330.4 = 19.4%, as SO_3 = 48.4%

Quantities are (ENCL. 5):

DDVP, 4%	674,000 l.
DDVP, 20%	489,000 l.
DDVP, 97%	389,000 l.
Fenitrothion (var. dilutions)	831,000 l.
Malathion, 95%	455,000 l.
Others	279,000 l.
TOTAL	3,117,000 l.

Pesticides listed as "Others" include: Karate, Decis 25, Sumithion, Diazinon, and Nonothion.

In addition to the 3 million l. of pesticide listed above, there are 2,600,000 l. solvent (Heavy Aromatic Naphtha, HAN) stored at the Ait Melloul depot. The HAN is intended for diluting the 389,000 l. of 97% DDVP which is stored at Ait Melloul, and mixing the two stocks would result in a mixture with about 20% DDVP by weight.

While all BHC should be destroyed, the situation is more uncertain regarding the other materials. Chemical analyses are under way to determine whether the materials are useable. Compounds which are not useable should be destroyed, compounds which are useable but not required by GOM should be sold or destroyed, and compounds which are useable and required by GOM should be repackaged if necessary and kept in appropriate storage.

CEMENT KILNS IN MOROCCO

Société des Ciments d'Agadir

Location: Route d'Essaouira, km 7.

Kilns: The plant operates two semi-wet kilns with Lepol grate preheater. Nodules are formed by pelletizing raw materials with water; nodules are then dried and preheated on a traveling grate preheater. Kiln systems are quite open and could probably receive an additional 1 kg. Cl per ton of clinker provided some electrofilter dust is discarded.

Ownership: Société des Ciments Français (France)

Pesticide Disposal: The plant, as an open kiln system, is technically well suited for burning chlorinated organics. As Agadir is a major tourist center, local authorities will probably oppose such an undertaking. The plant owner is expected to demand very high disposal fees for burning pesticides.

Société des Ciments de Marrakech "ASMAR"

Location: M'Zoudia, route d'Essaouria, km 45.

Kilns: One 1400 tpd preheater kiln with 5% bypass. The plant has been visited and will be described in detail below. In 1992 the kiln capacity will be doubled by adding a precalciner. After the kiln capacity has doubled, the present bypass system will no longer be adequate even for chloride added with raw materials alone.

Ownership: S.N.I., Abou Dabei, B.N.D.E., C.I.M.R., C.D.G., Lafarge Coppée (France), Société des Ciments Français (France).

Pesticide Disposal: Bypass has very little spare capacity and no filter.

Cimenterie nouvelle de Casablanca "CINOUCA"

Location: Douar Laaouameur, Caidat de Had Soualem, Cercle de Berrechid, Province de Settat, 40 km south of Casablanca.

Kilns: One 3000 tpd precalciner kiln. Chloride situation unknown.

Ownership: S.N.I., Lafarge Coppée, C.D.G., B.N.D.E.

Pesticide
Disposal: Probably not suited for chlorinated products.

Cimafsi

Location: Town of Safi, between Casablanca and Agadir.

Kilns: One 1600 tpd 5-stage preheater kiln to be started mid-1992.

Ownership: B.N.D.E., S.N.I., Société des Ciments Français.

Pesticide
Disposal: The chloride content of the raw materials is already higher than what normally is considered advisable for preheater kilns without a bypass. The kiln has no bypass.

Cementos Marroquis, C.M.A.

Location: Tamuda, Route de Torreta Meres, 5.8 km from Tetouan.

Kilns: Two small Lepol (grate preheater) kilns. Daily clinker output 500 tons, probably on one kiln only.

Ownership: Lafarge Coppée.

Pesticide
Disposal: Technically the kiln is well-suited for burning chlorinated waste. Plant owner will probably demand high disposal fees.

Cementos Tanger S.A.

Location: 17, Rue Rembrandt, Tangier. 8 km from Tangier.

Kilns: One wet process kiln, estimated production 500 tpd.

Ownership: Lafarge Coppée.

Pesticide
Disposal: Technically the kiln is well-suited for burning chlorinated waste. Plant owner will probably demand high disposal fees.

Société des Ciments Artificiels de Meknès (CADEM)

Location: Km 8, route de Fès, Meknès.

Kilns: One 2200 tpd precalciner kiln.

Ownership: S.N.I., Lafarge Coppée.

Pesticide Disposal: The kiln system can presumably not accept more chloride than is presently introduced with the raw materials.

Cimenterie de l'Oriental (CIOR)

Location: Oujda, km 45 RP1 Oujda - Fès.

Kilns: Two 1800 tpd preheater kilns without bypass. The plant was visited and will be described in detail below.

Ownership: O.D.I., B.I.D. (Djeddah).

Pesticide Disposal: Chloride input from the raw materials is already too high, resulting in operational problems. No further chloride input possible without installing a bypass.

Asment de Temara

Location: Ain Attig, Rabat.

Kilns: One 1650 tpd preheater kiln built by Fuller.

Ownership: S.N.C.E., B.N.D.E., C.M.K.D., C.D.G., S.A.I., B.I.D., S.F.I.

Pesticide Disposal: The kiln cannot accept more chloride than is already introduced with the raw materials.

VISITS TO CEMENT PLANTS

Société des Ciments de Marrakech "ASMAR"

The plant was visited on September 13, 1991. The kiln was originally equipped with a Buhler Miag preheater, but was later modified by CLE to operate as a normal 4-stage preheater kiln. It is anticipated that kiln capacity will double in 1992 by addition of an Onoda RSP precalciner built by CLE.

The kiln system is presently operating at the limit of its chloride capacity. Any additional chloride added would pass up the stack in the form of salt, resulting in a 30% increase in salt emission from the stack. If additional chloride intake were kept at 0.1 kg/t clinker, salt emission would increase by 15%.

When the capacity of the kiln is doubled by conversion to a precalciner, the amount of chloride to be removed via the bypass will also double. If the flow of bypass gas (std. m^3/hr.) is maintained at the present level, chloride concentration in the kiln gas will be doubled. This would happen automatically, as more than half the kiln fuel is burned in the precalciner, and kiln gas will represent less than half the total smoke gas from the system.

There is no difference between precalciner kilns and preheater kilns in terms of chloride circulation in the system and concentration in the material. The only difference is that evaporated chloride in precalciner kilns is contained in less than half the amount of kiln gas present in the preheater kiln.

The critical parameter in the formation of coating in the riser duct beyond the kiln is the chloride concentration in the gas phase, not in the solid material phase. The critical concentration is 12 grams of chloride per std. m^3 kiln gas. When doubling the output of a kiln, it is also necessary to remove twice as much kiln gas if chloride concentration in the kiln gas is to be kept at the previous level.

As ASMAR's kiln at M'Zoudia is going to be converted to a precalciner kiln next year (1992) it does not seem to make much sense to begin burning pesticides before that time. One reason is that the capacity of the kiln for burning pesticides is presently so low that it will not be possible to burn the entire stock of BHC before the kiln is shut down for modification; another reason is that burning chlorinated products in the kiln will increase salt emission into the atmosphere as long as the kiln has no bypass filter.

It is not recommended to plan even for a trial burn before the kiln is modified unless such a burn is necessary to convince plant owners and the surrounding community that the kiln can effectively handle pesticide disposal. There is already abundant evidence that a cement kiln can incinerate any organic compound with a Destruction and Removal Efficiency (DRE) better than 99.99%.

It is very strongly recommended that ASMAR be contacted and the entire situation explained to them in detail. If ASMAR is then amenable to burning pesticides in the kiln, it will be possible to make all necessary installations when the kiln is down for the already-scheduled modifications. These would include the larger

bypass with filter (which the plant needs in any case), a modified kiln burner, and probably upgraded instrumentation. The present gas analyser equipment consists of one analyser for O_2 and CO at the kiln inlet and one O_2 analyser after the preheater. The latter was not operating at the time of the visit.

Cimenterie de 'Oriental (CIOR), Oujda

The plant was visited on September 18, 1991. The kilns are two identical 4.6 x 72m 4-stage Polysius DOPOL kilns, each with a production capacity of 1800 tons per day.

The kiln burner is a Spanish-made Unitherm 3-channel burner, rather similar to the Pillard burner used at ASMAR. It also suffers from wear problems in the coal channel. The coal feeder is a Schenck SIMPLEX feeder which is not very accessible from the outside.

The raw mix is composed of 80% limestone with 0.01-0.015% Cl, and 20% clay with 0.025-0.035% Cl. The average raw mix contains 0.014-0.020% Cl corresponding to 0.22-0.31 kg Cl/t of clinker. As the Cl limit for 4-stage preheater kilns without a bypass is 0.23 kg/t clinker, this kiln is usually operating so overloaded with chloride that operational problems result.

The kilns are equipped with gas analysers for O_2, CO, and NO at the kiln inlet, and for O_2 and CO after the preheater.

Concentrations of volatile elements other than than Cl were:

	$\%SO_3$	$\%S$	$\%K_2O$	Na_2O
Raw mix :	0.1		0.7-0.9	0.15-0.25
Clinker :	0.3-0.7		1.3	0.15-0.20
Coal :		0.5-1.5		

The plant burns coal with Hi about 6000 kcal/kg clinker, and the fuel consumption is about 860 kcal/kg clinker.

As is evident from the above, the Oujda cement plant is not presently capable of burning chlorinated pesticides. Since the plant is owned by GOM and needs a bypass in any case (the pay-back time would be short, as operation of the plant would be much improved), and since the pesticide stocks are also owned by GOM, there ought to be a symbiosis possible in the form of sharing costs of a bypass installation by CIOR and GOM.

PESTICIDE DISPOSAL RATES

A bypass functions by maintaining the Cl concentration in gas leaving the kiln tube at a level not exceeding 12 g/std. m^3. All

Cl added in excess of upper limits for raw materials (0.23 kg/t clinker for 4-stage preheater kilns; 0.15 kg/t clinker for precalciner kilns) must be removed as bypass gas with Cl concentration of 12 g/std. m^3. The same amount of gas must thus be ultimately removed from either kiln system type in order to deal with a given amount of excess chloride.

Bypass capacity, expressed as a function of total chloride in kiln feed, is shown in ENCL. 6. A 5% bypass of total gas on a precalciner kiln is the equivalent of a 15% bypass of total kiln gas, as the kiln gas constitutes only about a third of the total gas. Reasons for this are that only 40% of the fuel is burned in the kiln tube, and that almost all CO_2 in the kiln feed is expelled in the precalciner.

Open kiln systems can also accept much more chloride without a bypass than closed systems. Inputs of 0.1% on clinker bases or 1 kg/t clinker are acceptable. Chloride still would need to be discarded as precipitator dust.

Some of the Morocco pesticides also contain phosphorus and sulphur, and there are limitations to inputs of these two elements.

Most Portland cements contain 0.05-0.25% P_2O_5, and there are no adverse effects on the cement at concentrations below 0.3% (up to 0.5% in some cases). Most cements will be able to accept an additional input of at least 0.1%.

Sulphur inputs are limited because of potential to form coatings on the riser duct beyond the kiln. Maximum sulphur inputs are a function of alkali inputs: sulphur in excess of amounts which can combine with alkalies will form $CaSO_4$. The $CaSO_4$, along with the alkali chlorides and alkali sulphates which are already present constitute eutectic salt mixes with low melting points.

As half the Na_2O introduced into a cement kiln will enter in solid solutions with the clinker materials, only half is available to combine with sulphur. On a stochiometric basis, excess sulphur in relation to alkali in:

$$SO_{3(excess)} = SO_3 - 0.85\ K_2O - 0.65\ Na_2O$$

Although it is best if there is no excess SO_3, up to 0.3% on clinker basis is acceptable for 4-stage preheater and precalciner kilns.

Sulphur is unlikely to cause operational problems in more open kiln systems--Lepol grate preheater kilns, wet process kilns, long dry process kilns; provided sulphur input is controlled so that SO_3 content of the clinker does not exceed 1.5%.

With knowledge of chloride, sulphur, and phosphorus inputs, along with bypass size (if present), it is possible to calculate how much of the three elements can be added in the form of pesticides or other hazardous materials:

Sample Calculation

It is desired to burn a mixture of a 45% solution of BHC in heavy aromatic naphtha and 95% undiluted Malathion in an 1800 tpd cement kiln with a 4-stage preheater and a 5% bypass for the kiln gas. The kiln is fed with a raw mix with following content of chloride, sulphur, alkali, and P_2O_5:

	Raw Mix	Clinker Basis
%Cl	0.020	0.031
%K_2O	0.85	1.33
%NaO	0.20	0.31
%SO_3	0.10	0.16
%P_2O_5	0.064	0.10
%Loss on Ignition(LOI)	36.0	0.0

Concentrations on clinker basis are calculated by multiplying raw mix concentrations be a factor of 100 : (100 - LOI).

The kiln is fired with coal which has an energy value of 6000 kcal/kg and a sulphur content of 1.5% S, corresponding to 3.75% SO_3. The specific heat consumption of the kiln is 860 kcal/kg clinker.

SO_3 added with the fuel is on clinker basis:
3.75 x 860/6000 = 0.54%, bringing the total SO_3 input up to 0.16 + 0.54 = 0.70%.

The sulphur excess can now be calculated:
$SO_{3(excess)}$ = 0.70 - 0.85 x 1.33 - 0.65 x 0.31 = -0.63%
The kiln can thus accept an extra SO_3 input of at least 0.6% (and probably up to 0.9%).

ENCL. 6 indicates that acceptable chloride intake at 5% bypass is about 0.06% on raw mix basis, corresponding to 0.094% on clinker basis. As the raw mix contributes 0.031% on clinker basis, the allowable extra input is 0.063% on clinker basis or 0.63 kg/t clinker.

Pure BHC contains 73.2% Cl; a 45% solution thus contains 0.45 x 73.2 = 32.9% Cl. Permissible addition X of the 45% solution expressed as percent of clinker production is thus:

X = 100 x 0.063 : 32.9 = 0.19%

With a kiln production of
1800 tpd = 75,000 kg/h =1,250 kg/min, the addition rate of 45% BHC solution will thus be 143 kg/h or 2.4 kg/min.

Acceptable addition of P_2O_5 to the clinker is 0.3 - 0.1 = 0.2% of the clinker. 95% Malathion contains 0.95 x 21.5 = 20.4% P_2O_5. Permissible addition Y of 95% Malathion is thus:

$$Y = 100 \times 0.2 : 20.4 = 1.0\%$$

SO_3 content of 95% Malathion is 46.0%, which means that a 1% addition on clinker basis will contribute 0.46% SO_3 to the clinker, which would be acceptable in the present example.

The BHC formulated as an 11% mixture with talc needs special attention. As talc adds MgO to the clinker and acts as an additional coal ash component, it is not recommended to feed this formulation at a higher rate than 1.25% of the clinker weight. This will add 0.1% Cl to the clinker.

HANDLING, MIXING, AND FEEDING OF LIQUID PESTICIDES

Most of the liquid pesticides in the Morocco stocks are stored in 200 l. steel drums and dispersed among a number of depots. They need to be transported to the cement plant and made suitable for handling by pumps and subsequent atomization into the kiln by a burner.

Transport from storage sites to the cement plant, or at least the first segment of the transport, should be done by tank truck. Drum contents should be filtered during transferral to the tank trucks. Filtering can be accomplished by placing a conical pump sump at each storage depot. Each of these would be covered by a strong metal grid on which drums are placed for emptying and possibly rinsing. A sieve with small openings is placed underneath the metal grid (openings with 0.5 mm. maximum diameter if the burner in the kiln has 1.0 mm openings). Two sieves in series should be used in case the upper sieve is damaged.

Solids removed by sieves can probably be mixed with the wheat bran containing 0.05% BHC, thus obtaining the characteristice of a free-flowing powder. The clean liquid can be pumped directly into the tank truck.

An appropriate receiving installation must be provided at the cement plant, and would consist of at least one receiving/mixing tank and one tank for feeding the mixed product to the kiln. The mixing tank should hold at least one week's pesticide consumption, depending upon the transport rhythm and need for mixing. The kiln feed tank needs to hold at least 3-4 days' consumption to avoid rapid changes in composition when transfers are made from the mixing tank to the kiln feed tank.

The kiln burner should be a conventional fuel oil burner lance with compressed air atomization. Openings should be no smaller than 1 mm. diameter to avoid blockages, and the burner lance

should fit inside the center guide pipe that accommodates the main oil burner used during heating up of the kiln. When coal firing is switched on, the main oil lance can be removed from the guide pipe. Oil burner lances with compressed air atomization are standard equipment and are available in many different sizes from a number of suppliers, including F.L. Smidth/Fuller.

It is beyond the scope of this report to present precise specifications for a liquid pesticide disposal installation in a cement plant. Such an installation would need to meet standards which apply to storage and handling facilities in chemical plants where the pesticides are produced. ENCL.7 presents considerations made in installing a waste-derived fuel system.

HANDLING AND FEEDING OF SOLID PESTICIDES

BHC in Morocco is stored either in paper bags (talc formulation) or jute bags (bran bait formulation). A number of the bags are broken, leaking, or too fragile to withstand transport. Whole bags and spilled powder can be transferred to containers (200 l. drums with lid) at the storage sites. The containers can then be transported by road or rail to the cement plant.

At the cement plant, containers are emptied into a shredder which reduces the full bags into small pieces for insufflating into the kiln along with the powder. The shredder installation should be placed directly on top of the silo or hopper from which the product is fed to the kiln. (An alternative would be a device which separates bags and contents.)

The silo should be placed on load cells, and extraction from the bottom of the silo done by a screw feeder. Feed rate is adjusted by altering the rpm of the feed screw, which can be calibrated in kg/h by means of the load cells supporting the weight of the silo.

If the powder and bags are separated, or if the bags are shredded into very small pieces (like confetti), the product can be fed directly to the suction side of the primary air fan. As it may be difficult to obtain such fine shredding, and as consequences for the burner will be disastrous if the axial air channel is blocked with pieces of bags (no cooling of the burner protruding into the kiln), it is probably safer to install a small separate blower that directly blows the shredded product into the kiln via a 3" pipe placed on top of the main burner and coated with refractory castable.

Small blowers capable of crushing and transporting reasonably soft materials are widely used on farms for crushing and transporting grain to be used as animal feed. They would easily handle wheat bran and talc (hardness 1 on Moh's scale).

The shredder and silo installation should be dedusted by the insufflation fan or primary air blower to avoid odors. Venting of the liquid pesticide tanks could also be done with the primary air blower.

HANDLING OF CONTAMINATED SOIL

There may also be as much as 1000 m^3 pesticide-contaminated soil from the Morocco pesticide depots. Contaminated soil is best collected in plastic-lined paper bags to avoid odors and trucked to the cement plant. Bags should not contain more than 25 kg. each to facilitate handling. The soil could be treated in a cement kiln in three different ways, provided that the introduction rate is kept low enough (below 1%) not to interfere with clinker quality.

a. Feeding into the back end of preheater and precalciner kilns. In principle, pesticides should be fed to the burning zone of a kiln rather than the back end. However, the technique is safe and adequate, given the low concentrations and the possibility of feeding the soil in closed steel drums into the back end of the kiln, delaying the liberation of the pesticides. A cement producer might object to the idea of feeding coarse or concentrated "shots" of clay component into the kiln; and if the kiln has a bypass, distance between introduction point and gas take-out is very small.

b. Feeding between kiln and cooler on all kilns. A better solution is probably feeding the soil between kiln and cooler where it will meet hot clinker of at least 1200°C. Feeding can be either continuous via a small water-cooled screw feeder, or soil could be dumped into the cooler in small bags. Organic material introduced on top of the hot bed of clinker will burn and combustion products will be carried up into the burning zone of the kiln by the hot secondary air and heated to about 2000°C.

c. Introduction into the burning zone by pneumatic gun. A third possibility is to pack the soil into 25-50 l. cardboard drums and shoot them pneumatically into the burning zone of the kiln. F.L. Smidth manufactures a patented device of this type known as the "Gunnax" system, but it is probably an over-elaborate alternative for the present purpose.

SAFETY MEASURES RELATING TO KILN OPERATION

Prerequisites for safe destruction of pesticides are that the kiln is in steady operation, that the burning zone is hot enough, and that an adequate air excess is present.

The kiln must be equipped with gas analysers measuring the O_2 and CO content at the end of the kiln tube. If readings of these instruments fall outside the permitted range, the feed of pesticides to the kiln must automatically stop (which also applies if the instruments fail). On preheater kilns it is also advisable to have O_2 and CO analysers placed after the preheater.

Temperature of the clinker/secondary air should be measured by a thermocouple placed under the main burner or by a two-color radiation pyrometer. If the reading is too low, the pesticide feed must stop automatically. Similar electrical interlockings may be made for the kiln motor torque and NO-meter (both good indicators of burning zone temperature), primary air pressure, kiln back end temperature, and any other relevant parameter. Loss of primary fuel must cut the pesticide feed immediately.

RECOMMENDATIONS

As a first step, the Government of Morocco must decide which pesticides are to be kept or sold, and which are to be destroyed. Once the decision has been made, it is suggested that GOM contact the following cement producers:

1) Cementos Tanger SA
2) Cementos Marroquis, C.M.A.
3) Société des Ciments d'Agadir
4) Société des Ciments de Marrakech "ASMAR"
5) Cimenterie de l'Oriental (CIOR)

Plants 1) and 2) are owned by Lafarge Coppée, which in turn own 100% of the shares in SYSTECH, the largest supplier of waste fuels for the United States cement industry. There is no doubt that Lafarge Coppée and SYSTECH together could resolve the entire obsolete pesticide disposal problem in Morocco on a turnkey basis, including collecting pesticides, transporting them to the cement plant, providing all necessary installations at the plant, incinerating the pesticides, monitoring emissions from the kilns, and managing laboratory control and safety aspects of the project--all of the above at a price, of course.

The Agadir plant is mentioned because the kilns are technically appropriate and because the plant is located near the main pesticide depots. The plant's location in the middle of a tourist center may rule out its use for incinerating pesticides.

The ASMAR and CIOR plants both need new bypass installations in order to cope with the burning of chlorinated waste, but will be able to do so if the necessary bypass capacity is installed. The two cement producers will probably be interested if GOM shares in the cost of the installation.

Copenhagen, 27th September, 1991

Torben Enkegaard

ENCL. 1

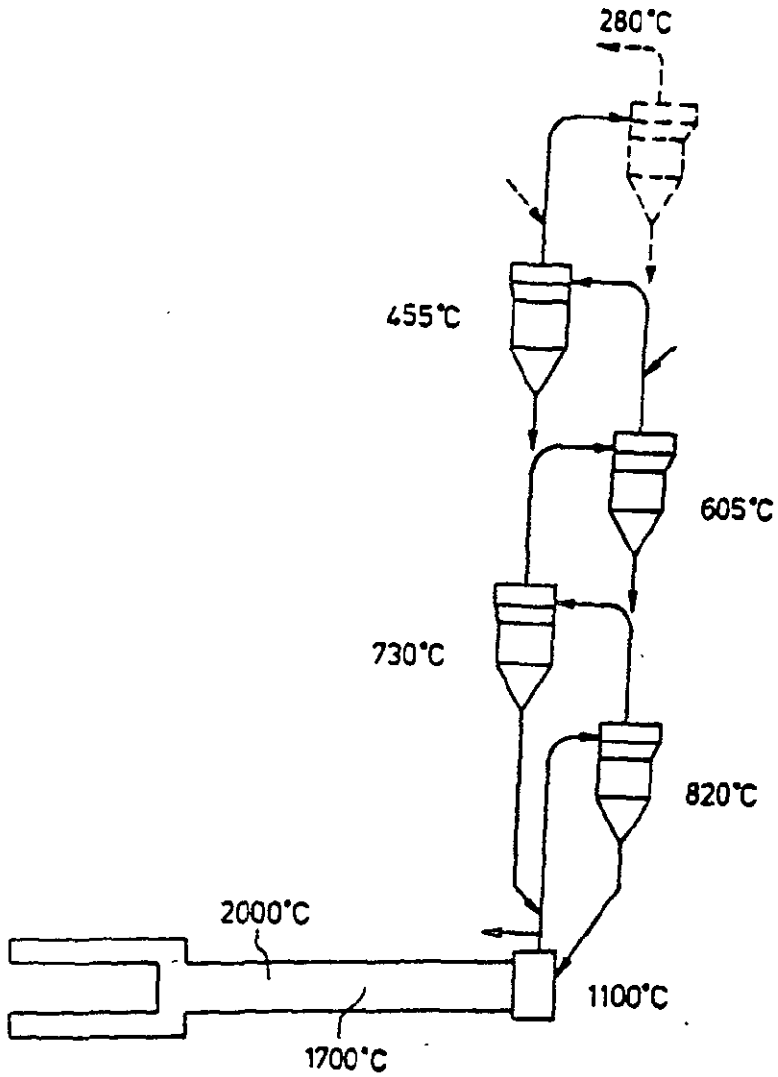


Fig. 1A

ENCL. 2

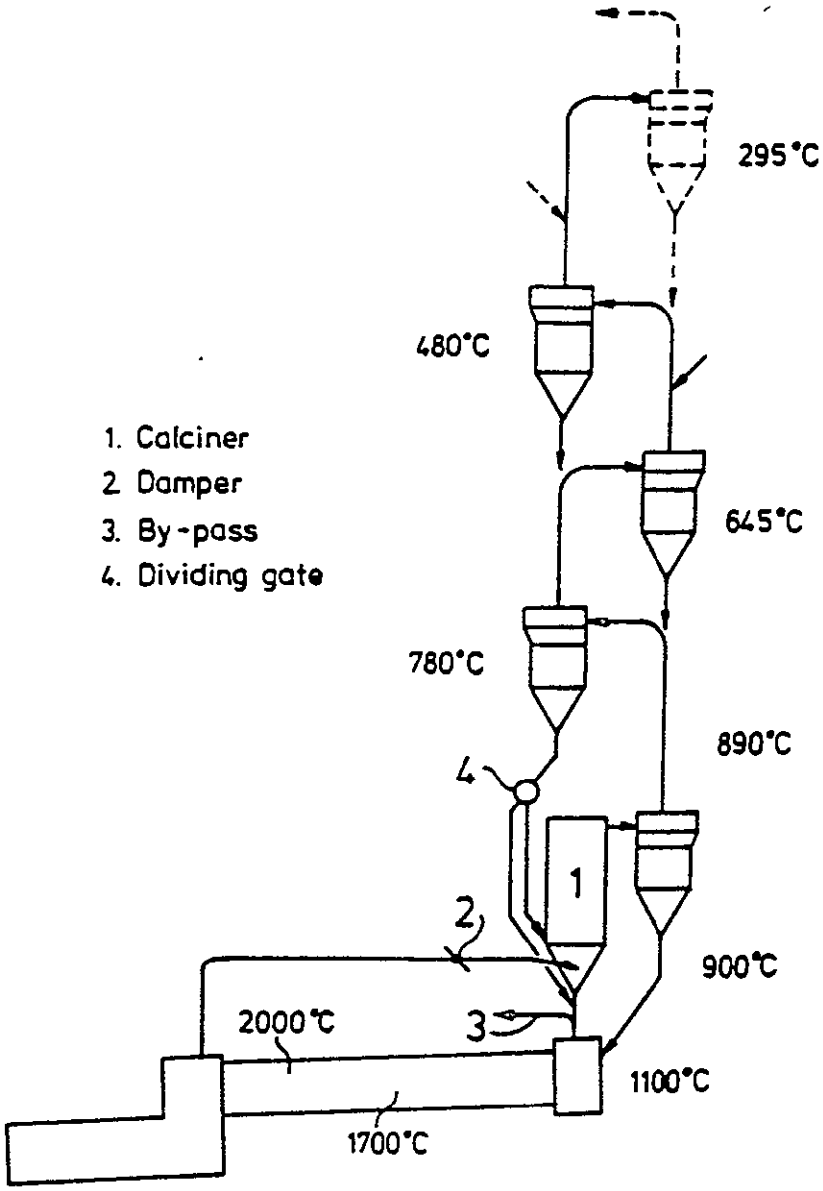

295°C
480°C
1. Calciner
2. Damper
3. By-pass
4. Dividing gate
645°C
780°C
890°C
4
1
2
900°C
2000°C
3
1100°C
1700°C

Fig. 1B

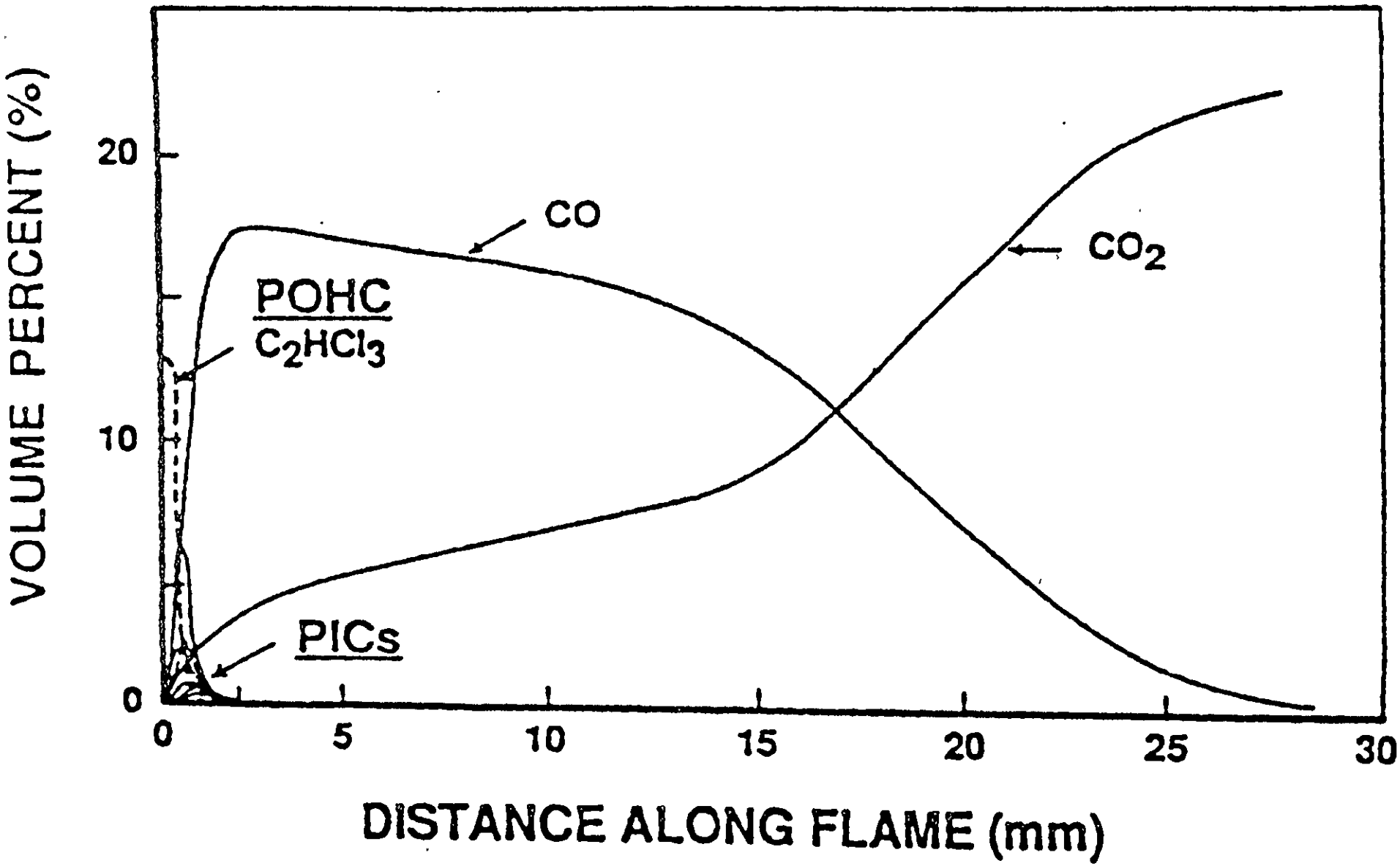


Figure 2. POHC and PIC profiles inside a premixed flame. Source: Senkan, IIT.

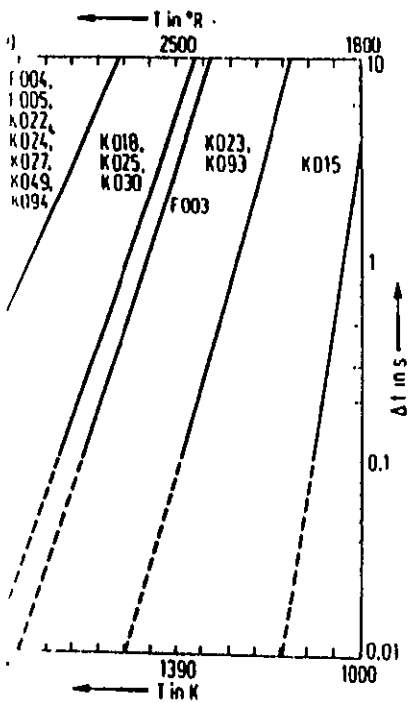
ENCL. 3

here: A = Arrhenius pre-exponent frequenc factor (S^{-1})
E = Energy af activation (J/kg-mole)
R = Universal gas constant (8314 J/kg-mole-°K)
T = Absolute temperature (°K).

If the A and E values are known the required retention time can be calculated for elected temperature (and visa versa).

The retention time-temperature relationship for some organic compounds mentioned in Section 2.1.2 is shown in Fig. 3.1.

Some organic compounds are shown in Table 3.1 in order of destructability [11].



. 3.1. Plots of time-temperature requirements for 99.99 per cent destruction of selected ardous waste categories. (US, EPA, April 1983)

1 Toxic Wastes, Which can be Incinerated

many organic toxic wastes such as pesticides the incineration process if often most practical destruction alternative.

the temperature and residence time has been selected correctly the destruction be almost complete.

ompounds containing toxic metals (for example mercury) pose a problem however. h waste might be treated by special thermal methods pyrolysis or distillation. ercury containing wastes are incinerated special flue gas cleaning systems should sed.

Table 3.1. Order of inc sing destruct ility based on temperature required for 99.99 percent dest on at 1-sec residence time [11]

Order	Compound	Temperature[a] C	(F)
1	Methyl chloride	844	(1550)
2	Methane	836	(1535)
3	Phenol	807	(1484)
4	Methylene chloride	797	(1466)
5	Pyridine	791	(1455)
6	Chlorobenzene	768	(1413)
7	Dichlorobenzene	765	(1408)
8	Hexachlorobenzene	763	(1405)
9	Ethane	761	(1401)
10	Vinyl chloride	746	(1374)
11	Ethyl chloride	737	(1358)
12	Benzene	737	(1358)
13	Cresol	722	(1331)
14	Ethylene	721	(1329)
15	Toluene	720	(1327)
16	Nitrobenzene	720	(1327)
17	Hexachlorobutadiene	719	(1325)
18	Trichlorobenzene	716	(1320)
19	Vinylidene chloride	712	(1313)
20	Acetophenol	711	(1310)
21	Propane	708	(1305)
22	1,2,2-trichloro-1,1,2-trifluoroethane	692	(1277)
23	Dichloropropane	686	(1266)
24	Trichloroethane	683	(1260)
25	Phthalic anhydride	672	(1240)
26	Isobutanol	666	(1229)
27	Trichloroethylene	662	(1222)
28	Naphthalene	661	(1221)
29	Methyl ethyl ketone	657	(1213)
30	Dichloroethane	656	(1212)
31	Epichlorohydrin	618	(1143)
32	Maleic anhydride	607	(1123)
33	Bis(2-chloroethyl)ether	602	(1115)
34	Methyl isobutyl ketone	599	(1109)
35	Trichloropropane	571	(1060)
36	Benzotrichloride	528	(982)
37	Carbon disulfide	400	(751)

a Temperatur required for 99.99 per cent destruction at a residence time of 1 second.

3.3 Toxic Wastes Which can be Detoxified

3.3.1 Inorganic Toxic Wastes

Among the wastes which can be detoxified by chemical methods, the cyanide or chromate containing wastes originating from metal plating industry should be mentioned.

ENCL. 4

ANNEXE 5.4.

PESTICIDE STOCKS IN MOROCCO

REGION : OUJDA

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
TRARID	DDVP 4 %	6.150		
BASSIA	"	4.000		
CHOUATER	"	3.000		
B. TADJIT	"	2.200		
BOUARFA	"	52.130		
BOUANANE	"	9.980		
TALSSINT	"	7.400		
BOUDNIB	"	6.050		
FIGUIG	"	6.060		
FIGUIG	" 20%	9.000		
TALSSINT	"	9.400		
BOUANANE	"	5.900		
BOUARFA	"	26.650		
B. TADJIT	"	5.600		
TRARID	"	5.600		
BOUARFA	NOV	3.600		
BOUARFA	FENITH.DIL.	800		
BOUARFA	MALATH.PUR	16.000		
BOUARFA	" DIL.	1.400		
BOUDNIB	MALATHION	3.000		
BOUDNIB	KARATE	120		

DDVP = DICHLORVOS

REGION : ERRACHIDIA

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
TINEJDAD				
JORF				
RISSANI				
GOURRAMA				
RAMLIA				
TAOUZ AMERZ.				
FEZOU				
OUMJRAN A.S.				
AMELLAGO A.				
IFEGH (AGHB)				
IFEGH				
TOUROUG				
ERRACHIDIA	DDVP	2.600		
ERRACHIDIA	" 4%	5.190		
BPA ERRACHIDIA	"	6.200	60 600	
TAOUZ	"	9.200		
ERFOUD	"	8.300		
RICH	"	11.640		
GOULMIMA	"	10.755		
ALNIF	"	6.750		
RICH	" 20%	6.950		
ERFOUD	"	10.800		
TAOUZ	"	7.200	55000	
ALNIF	"	6.800		
GOULMIMA	"	9.000		
BPA ERRACHIDIA	"	14.120		
BPA ERRACHIDIA	FENITHROTION			
GOULMIMA	"	200		
BPA ERRACHIDIA	" 35%	200		
BPA ERRACHIDIA	MALATHION	7.000	14000	
ALNIF	"	2.000		
ERFOUD	"	3.000		
RICH	"	300		
GOULMIMA	"	1.700		
RICH	KARATE	74		
GOULMIMA	"	132		
BPA ERRACHIDIA	"			
BPA ERRACHIDIA	SOLVANT	2.000		
TINGHIR				

REGION : MARRAKECH

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
AMIZMIZ	DDVP 4%	400		
TAHANAOUT	"	400		
A.OURIR	"	400	5537	
IMINTANOUT	"	1.490		
MARRAKECH	"	400		
S.RAHAL	"	400		
MARRAKECH	" 20%	3.000	3000	
"	PENITH. 10%	1.000		
"	MALATH. 95%	3.200	3200	
"	DECIS 25	5.375		
TAHANAOUT	"	500		
S.RAHAL	"	500		
AMIZMIZ	"	500		
IMINTANOUT	"	500		
A.OURIR	"	500		

REGION : SAFI

LOCALITE	NATURE	QUANTITE	CONCENTRATIN	OBSERVATIONS
ESSAOUIRA	DDVP 4%	3.680	3700	
ESSAOUIRA	DECIS 25	1.500		

REGION : OUARZAZATE

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
SKOURA				
K. MEGOUNA				
BOUMALENE				
TAGOUNITE				
AGDEZ				
ZAGORA				
F.ZGUID				
TAZNAKHT				
TALIOUINE				
TAGHBALT				
N'KOBE				
TAZARINE				
M'HAMID				
OUARZAZATE TAMETK	DDVP 4%	35.075	3.500	
OUARZAZATE TAMETK	" 20%	89.220	89.220	
OUARZAZATE	FENITH. 50%	5.170		
OUARZAZATE	MALATH. 96%	47.210	47.210	
OUARZAZATE	SUMITH.100%	400		
OUARZAZATE	DECIS	1.200		

REGION : AGADIR

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
IGHREM	DDVP 4%	15.200		
A K K A	"	12.400	66500	
F.EL HISSEN	"	2.200		
F.EL HISSEN	"	36.550		
A K K A	" 20%	14.800	69000	
F.EL HISSEN	"	26.800		
IGHREM	"	17.400		
F.EL HISSEN	FENITH. 7%	1.200		
F.EL HISSEN	" 30%	2.000		
F.EL HISSEN	MALATH.14%	3.800		
IGHREM	" 96%	4.400	103500	
A K K A	"	9.600		
F.EL HISSEN	"	31.550		
A S S A				
A S S A	DDVP 4%	3.266		
TAFRAOUT	"	9.250		
A N Z I	"	550	48000	
SIDI IFNI	"	2.200		
GUELMIM	"	31.800		
TIZNIT	"	1.000		
GUELMIM	" 15%	7.000	51000	
GUELMIM	" 20%	36.800		
SIDI IFNI	"	7.400		
TAFRAOUT	FENITH. 35%	160		
GUELMIM	" 50%	19.200		
TAFRAOUT	" 96%	1.900		
SIDI IFNI	MALATH. 96%	3.200		
TAFRAOUT	"	7.800		
A S S A	"	8.000	42000	
TIZNIT	"	9.400		
GUELMIM	"	13.800		
GUELMIM	KARATE	5.775		

REGION : AGADIR (SUITE)

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
A. MELLOUL	KARATE	90.250		
"	DDVP 4%	6.000		
"	" 20%	15.600		
"	" 97%	389.000		
"	MALATH. 96%	227.400		
"	SOLVANT	2.600.000		
"	DECIS 12,5	52.100		
"	DECIS EC 25	112.400		
"	FENITH. 500	280.000		
"	" 500 EC	17.400		
"	" 1000	480.000		
TAN TAN	DDVP 4%	6.800		
"	" 20%	24.700		
"	FENITH.35%	1.700		
"	MALATH.96%	28.000		

REGION : LAAYOUNE

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
LAAYOUNE	DDVP 4%	52.170	[illegible]	
"	" 20%	78.100	[illegible]	
"	MALATH.95%	23.400	[illegible]	
"	DIAZINON	1.800		
"	DECIS	1.800		
"	FENIT.1000	2.460		
"	DDVP 20%	3.275	[illegible]	
DAKHLA	DDVP 4%	266.000	[illegible]	
"	" 20%	8.000	[illegible]	

REGION : FES

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
MISSOUR	DDVP 4%	12.500	[illegible]	
"	" 20%	17.000	[illegible]	

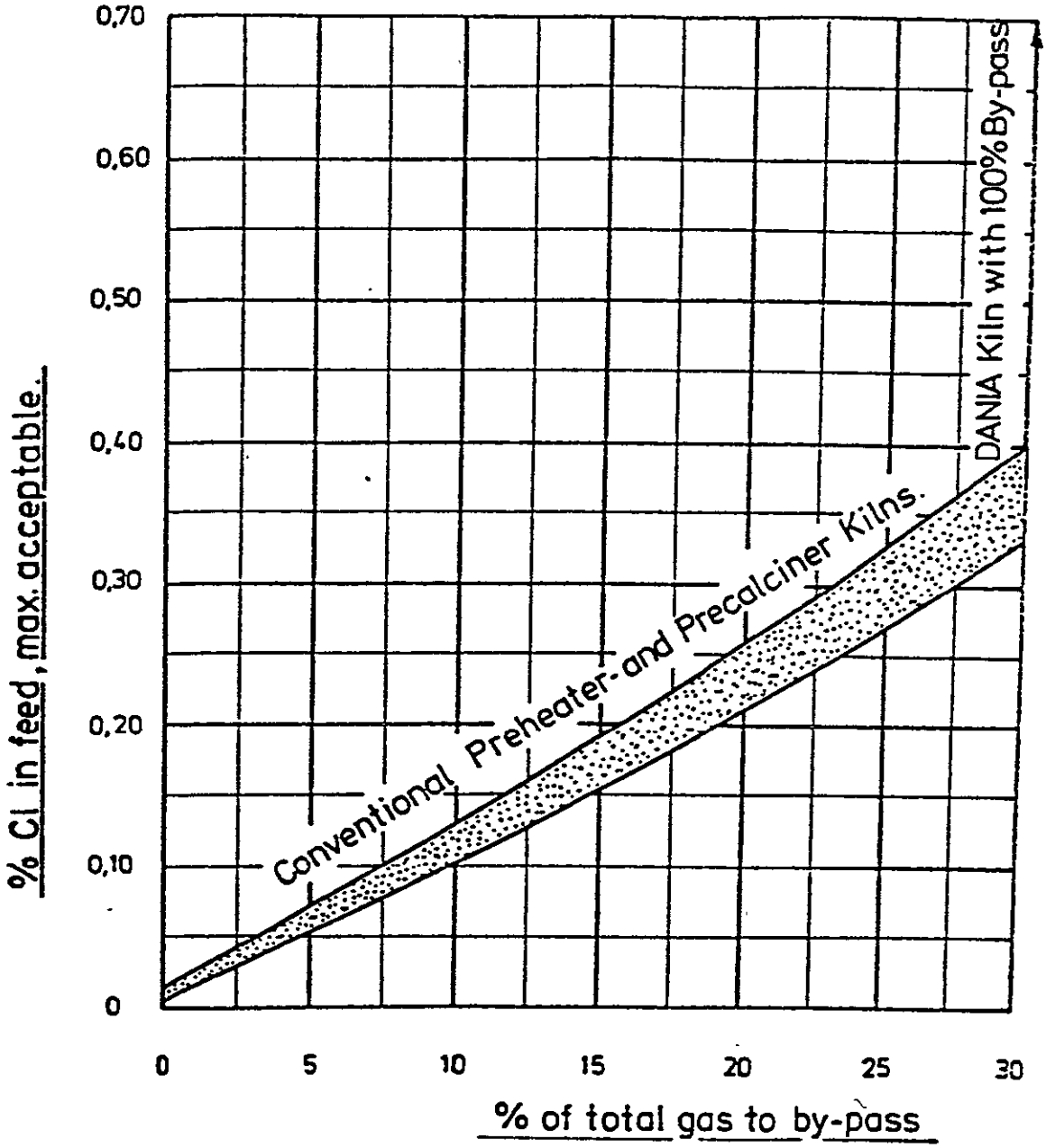
REGION : MEKNES

LOCALITE	NATURE	QUANTITE	CONCENTRATION	OBSERVATIONS
KHENIFRA	DDVP 4%	16.600	16600	
"	" 20%	13.500	13500	
"	DECIS ULV	2.500		
"	DECIS	1.550		

Kiln Processes.

VOLATILE MATTER

By-Pass. Reduction of Chloride Circulation.



By-pass designed to reduce the chloride concentration in kiln exit gas to an acceptable level (12 g Cl/Nm³ kiln exit gas).

HOW TO INSTALL A WASTE SYSTEM

by Hubert L. Smith

An expert in the field gives tips on how to install an economic, environmentally acceptable waste-derived fuel facility in a cement plant

When a waste-derived fuel (WDF) system is installed in a cement plant, it must satisfy a variety of needs. It must:

- Provide a means of disposal for unwanted material;
- Be compatible with the manufacture of cement;
- Meet federal, state, and local regulations;
- Provide a reasonable return on investment for all involved.

Since a WDF facility exists primarily to reduce the impact that hazardous material may have on the environment, it is essential that each facility be operated in a manner that minimizes leakage, spillage, evaporation, runoff, and other detrimental occurrences that would adversely affect the environment. The concept and design of a WDF facility and its components are the critical aspects of an economical, environmentally acceptable system. It is the responsibility of the owner, engineer, and contractor to design and build an operator-friendly system and reduce any chance of environmental contamination.

Most WDF facilities have six basic components:

- Transport vehicle unloading;
- Material handling/control;
- Waste material storage;
- Material processing;
- Fuel blending;
- Fuel burning.

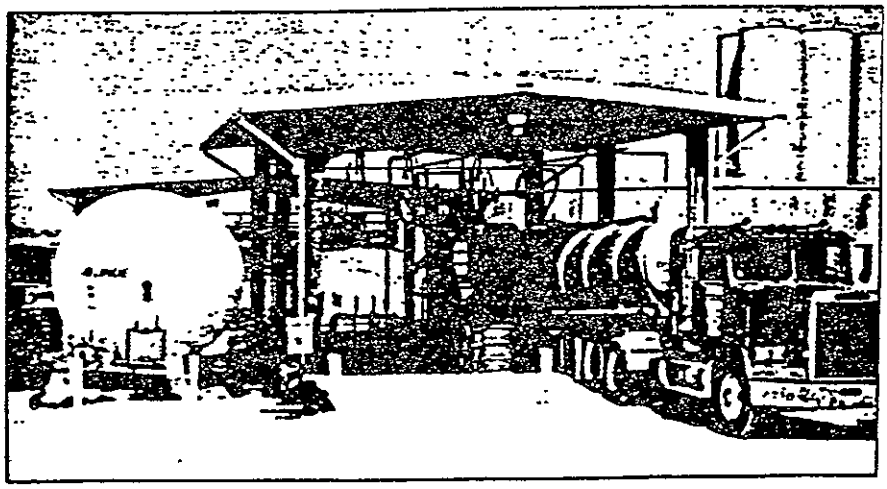
Each of these components offers an opportunity for technical excellence in design and operation, and each offers a different potential for problems and liability issues. The proper combination of these components provides the basis for a successful facility.

TRANSPORT vehicle unloading plays a major role in most WDF facilities. For instance, it is the bulk truck and railcar unloading areas that set the "feeling" for non-company individuals about the entire facility. If truck drivers have a clean facility in which they can easily unload, they will spread positive feedback to others. In an industry which often conjures up negative images, positive public relations can be helpful.

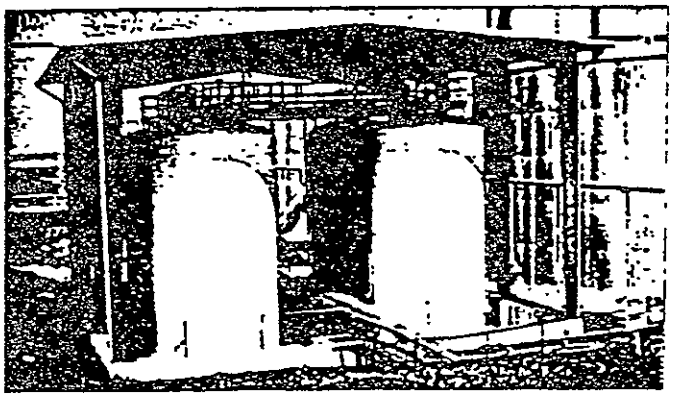
It is important that unloading areas with adequate spill containment be provided for each type of material shipment that is received. Zones that are impervious to the material being handled and that are capable of impounding the entire content of the transport vehicle need to be established. Crack control must be a prime ingredient in the spill containment design, and concrete containments that hold liquids need to be steel-lined, since concrete is porous to many solvents.

Pumps and strainers should be located where the length of the pump suction line is minimized,

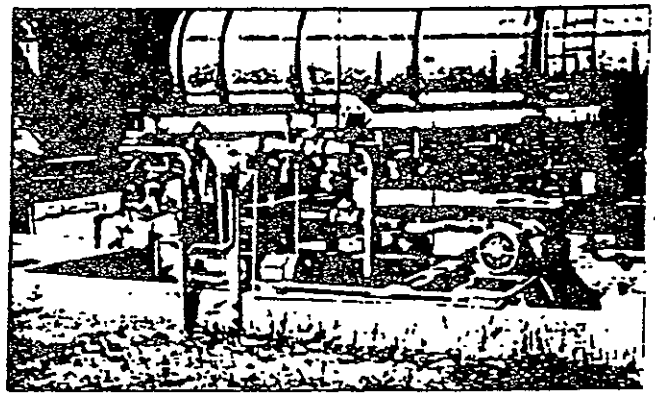
This two-bay truck unloading area is covered to protect it against the hazards of inclement weather, specifically rain, which must be contained and disposed of in a manner other than discharging outside the compound.



Hubert L. Smith is president of the Texas Division of the Benham Group, in Dallas, Texas. This article is a condensation of a paper he presented at ROCK PRODUCTS' 25th International Cement Seminar in Los Angeles, Calif., in Dec. 1989.



These large 40,000-gal storage tanks provide the opportunity for blending for consistent chemical/moisture content and heat value, causing fewer upsets in the kiln.



Pumps, such as those at this auxiliary truck unloading pump station, should be selected realizing that the viscosity of the received fuel may vary greatly.

and the strainers can be easily cleaned. Pumps should be selected with the knowledge that the viscosity of the received fuel may vary greatly, and that some fuel may contain solids. Strainers should be selected for ease of cleaning, since the fuel that passes through is waste. Some fuel may have sufficient solids or a consolidated mass to justify the installation of sizing devices. However, in many fuels, the solids have higher calorific values than the liquids; therefore, the solids should not be arbitrarily strained and thrown away.

Consideration should be given to covering unloading areas in locations with inclement weather, because all rain water must be contained and disposed of in a manner other than discharging outside the compound. Employees working under cover are also more likely to perform necessary tasks more accurately.

By furnishing drive-through truck unloading, a WDF facility can enhance the safety of vehicle operators and facility personnel. Drive-through truck unloading also negates the hazards associated with backing a vehicle and provides protection for railcars spotted for unloading.

If on-site material sampling is to be performed, a truck staging area should be provided. This allows material sampling (about a 2-hr process) to be performed without clogging the unloading area. Fuel recirculation through the railcar is a good idea as well, since solids tend to settle on the bottom of the car after it has been on the tracks for a long period of time. The material test sample will be more indicative of the entire carload if taken after the recirculation process.

HAZARDOUS waste material handling and control is another basic component of a WDF facility, and pumps, strainers, sizing devices, piping, control and isolation valves, and flow rate detection are the key ingredients in such a material-handling system.

The variability of the waste fuel's viscosity and solids content offers an interesting challenge in pump selection. A variety of pump types have been tried—including centrifugal, gear, and positive displacement—to handle the low head/high flow rate for unloading and transfer between tanks, and to handle the controlled high head/low flow rate required for kiln feed. The centrifugal pump seems to be the best suited for providing the necessary flexibility, even though it may be less efficient in certain applications.

Pump seals must be carefully chosen to provide protection against leakage. The type of seal used affects the organic emission rate claimed in the Resource Conservation and Recovery Act permit and the environmental cleanliness of an operation.

Sizing devices are normally grinders. Again, several types have been tried through the years. Some grinders provide pumping action with sizing, which requires closer internal tolerances, while others are aimed at low-maintenance, coarse operations.

Piping is critical in a material-handling system, because its layout can prevent potential plugging. Suction lines should be kept as short and straight as possible; discharge lines should be routed so that there are no traps in which solids can concentrate; and if a trap is needed, a method to clean it must be provided.

Waste material flow control can be provided by remote or manually operated isolation valves. (For remote operation, monitoring devices can be installed to assure that flow is occurring in desired locations.) All valves and pipe flanges must be located within a containment area, or containment must be furnished in some other manner.

Since WDF is a waste product, there is normally solid material within the fuel which will foul the pipeline if any device protrudes into the flow. Therefore, flow rate and pressure detection must be obtained with non-intrusive devices, such as open tubes or external mechanisms. Flow rate and pressure control may be accomplished by variable pump speed or a pressure-relief recirculation system. A recirculation system can return the fuel to a tank or to the suction side of the pump for viscosity reduction.

Installing A Waste System

WASTE material storage, another component of a WDF facility, can normally be accomplished in carbon steel tanks, if the fuel is organic. The corrosivity of most compounds found in WDF is such that the small amount of additional metal required for an acceptable tank life is economically justifiable. Most regulatory agencies require tanks to have double steel or raised bottoms which allow visual inspection for leakage.

Top- or side-mounted agitators should be provided in each storage tank to reduce settlement and potential plugging. Top-mounted units have larger shaft diameters and propellers, but require less horsepower and have no seal leakage. Side-mounted units require multiple agitators with higher horsepower and demand special attention to prevent seal leakage.

Multiple storage tank sizes can provide many benefits. Large tanks provide good blending for consistent chemical/moisture content and heat value, causing less upsets in the kiln. Medium-sized tanks provide separated storage of inconsistent and compatible fuel until it can be properly blended, allowing more variety in acceptable material. Small tanks provide storage and feeding of incompatible fuel. A complete tank farm which is to receive unblended fuel has tanks of various sizes to accommodate the expected WDF variability and throughput.

One of the problems encountered in waste material storage is that of volatile organic compound (VOC) vapors, which are emitted by thermal breathing and tank filling. Techniques such as floating roofs, nitrogen blanketing, carbon absorption, and flares can be used to combat this.

CONTAINER storage and material processing from containers is a relatively new field for hazardous waste material facilities in the cement plant. Techniques for emptying and cleaning containers and processing waste to a pumpable state are being continually developed and improved.

Storage and warehouse facilities must meet stringent environmental and fire-safety codes dictating pile sizes, stack height, building construction, room ventilation, fire protection, pile spacing, and aisle widths.

Furthermore, the facility must be designed to provide spill containment for a code-specified percentage of total storage. This containment must minimize exposure of non-leaking containers to spills, as well as safely contain the spilled material until it can be removed. It is imperative that the storage arrangement allows visual inspection of each container.

Codes governing the geographical area in which a WDF facility is being built will dictate the level of ventilation required for the warehouse. It must be remembered that most WDF vapors are heavier than air and settle to the floor; therefore, a ventilation system which will adequately sweep the floor, as well as provide proper temperature control ventilation during the summer, is highly recommended.

All electrical and material-handling devices must be chosen for compatibility with explosion-proof construction. Partition walls and connecting doors between separated portions of the warehouse must meet a code-dictated fire rating. This can make fork lift operation difficult, if the facility is not properly designed.

Material received in drums and portable containers may be in liquid, sludge, or solid form, so the processing area must be designed to handle material in any of these manifestations. Whether material is removed from its container by shovel and bucket or by automated equipment, certain basic design criteria must be considered (i.e., fire protection, spill containment, room ventilation, personnel safety from splashing, and VOC vapor control).

As with the warehouse area, the processing area's fire protection, room ventilation, and spill containment criteria are code-dictated. To bolster personnel safety, a decontamination area should be engineered into the facility to allow employees access to a shower and clean clothes if spill contamination should occur. Safety showers and eye washes should also be located in the processing area.

Whether the material is mixed in and pumped from the container or emptied into a separate mixing vessel, the used container must be properly handled. The choices seem to be to completely clean the container, clean it sufficiently for return to the waste generator as a recycled container, or dispose of it by shredding, by burning, or by landfilling.

The technique of processing material from containers will receive close attention in the near future. It is an area of good potential return for invested capital.

WASTE-derived fuel has been used successfully to fire rotary cement kilns in amounts as low as 10% of the total fuel to as high as 100% of total replacement for other fuel. Current installations have placed the WDF torch in locations both inside and outside the coal pipe. External torches have been placed in various sectors of the kiln hood, most with great success.

The torch tip can be a simple, single-hole tip when the fuel is supplemental to a main fuel, but it should be designed to accommodate compressed air that can be used for swirl and atomizing air when needed. The fuel and atomizing air must have flow and pressure control. Fuel pressures in systems with simple torch tips vary from 50 to 70 psi, with some as high as 120 psi, depending on the system design and the amount of atomizing air used.

If the current trend toward using the rotary cement kiln as an environmentally safe burning device for hazardous waste continues, a WDF facility will become an integral part of every cement plant. A well-designed, properly constructed, meticulously operated plant will be essential to maintain the positive feelings the environmental community has toward the cement industry. ■