



Project Summary

Engineering Assessment of EDB Pesticide Destruction Technologies

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Under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act, the U.S. Environmental Protection Agency (EPA) suspended and cancelled the registrations and prohibited the further use, sale, and distribution of ethylene dibromide (EDB) pesticide formulations. As a part of this ban, EPA also assumed the responsibility for destroying/disposing of existing EDB stocks.

The project covered by this report involved an engineering evaluation of the suitability of various available technologies for the destruction of ethylene dibromide pesticides. The purpose of the study was to highlight the technical merits and shortcomings, safety, cost, and total time requirement for each of the alternatives considered.

Both thermal and chemical destruction options were considered. Evaluation criteria were developed so that the different options could be compared on a common basis. Information was collected on each candidate process through a literature search and discussions with industry experts. Concurrent with these efforts, bench-scale tests of the chemical methods were conducted. Also, a test burn was made at a commercial facility to determine the effectiveness of one of the incineration options. The results of these tests were factored into this report. Because the chemical processes are still in the conceptual stages, only preliminary process calculations and cost estimates were developed for these processes.

Based on the results of this study, incineration in the presence of sulfur dioxide appears to be the best alternative for the safe, effective, rapid, and economical destruction of the ethylene dibromide pesticides.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In September 1983 and February 1984, the U.S. Environmental Protection Agency (EPA) suspended the registrations of ethylene dibromide (EDB) pesticide formulations. Later, further use, sale, and distribution of these formulations were prohibited. This action was taken under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). As part of this regulatory action, the EPA issued orders that halted the use of EDB-containing material and requested manufacturers and distributors to recall all existing EDB products. The EPA was also required to indemnify all registrants and other owners of EDB pesticides for their economic losses and to take responsibility for the destruction/disposal of the EDB stocks.

The quantity of formulated EDB pesticides identified for disposal totalled approximately 346,000 gallons or 3.7 million pounds, 1.1 million pounds of which was actually EDB. For purposes of background information, the various EDB formulations are divided into four cate-

gories. These categories and their associated approximate quantities are shown below:

Category	Quantity, 10 ³ gallons
1. CS ₂ -containing formulations	132
2. Chloropicrin-containing formulations	70
3. Methyl bromide-containing formulations	19
4. Miscellaneous formulations	125

Technical Approach

The efforts of this study were focused on the following steps:

1. An engineering evaluation was made, which involved the identification of candidate technologies and processes, the development of selection criteria, and the application of selection criteria to support technical judgments.
2. Vendor contacts were made to the various incineration facility operators to determine interest, feasibility, and cost to destroy the EDB formulations.
3. Preliminary process designs and cost estimates were developed for the selected chemical destruction processes in order to compare these processes on an equal basis.
4. Process design and cost packages were developed by working closely with the EPA process developers. Bench-scale performance data were used to support equipment design and operating assumptions.
5. The results of a parallel bench-scale laboratory study were factored into the analysis to support and expand the EPA bench-scale work.
6. A trial burn of two EDB formulations was separately contracted for by the EPA to obtain more information on incineration in the presence of sulfur dioxide (SO₂) to facilitate bromine scrubbing. Data from this test were then factored into the evaluation of all alternatives.

Evaluation Criteria

The aim of the evaluation was to highlight the technical merits and shortcomings, safety, cost, and total required time for each of the alternatives considered. To provide a common basis

to compare different process options, the following evaluation criteria were developed in consultation with the EPA:

- Status - Commercial, Pilot Scale, or Conceptual
- Accessibility
- Past Experience
- Need for Development and Testing
- Preprocessing
- Process Safety
- Toxic Emissions
- Residues
- Need for New/Additional Equipment
- Extent of Corrosion
- Process Compatibility with Pesticides
- Secondary Environmental Impact and Health Considerations
- Mechanical Reliability
- Transportational Access to Facility
- Storage and Handling of Pesticides and Residues
- Cost
- Permitting
- Probability of Success
- Time for Completion

Information was collected on each candidate process so that each item in the evaluation criteria could be addressed. This entailed an exhaustive literature survey, discussions with industry experts, process calculations, and preliminary cost estimates.

Cost Estimating Procedure

Process economics is an important factor in the ultimate selection of a technology. For comparison of the cost-effectiveness of each option, unit costs (\$/lb of pesticide) were established for each process option. Unit costs for technologies already commercialized (incineration and cement kiln incineration) were obtained by contacting vendors for their best possible estimates. With regard to chemical destruction, both available process options available are still in the conceptual stages. Based on laboratory-scale results, preliminary flow sheets were developed, and then preliminary process design and preliminary cost estimates were made.

Technologies Evaluated

The following technologies were selected in this engineering evaluation as possible candidates for the elimination of EDB pesticide formulations:

- (1) Incineration in a waste incinerator under oxidizing (excess air) conditions (conventional incineration)

- (2) Starved-air incineration
- (3) Incineration in the presence of sulfur dioxide or sulfur-containing waste
- (4) Incineration in a cement kiln
- (5) Chemical destruction by the ATEG process
- (6) Chemical destruction with the zinc process

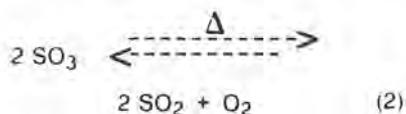
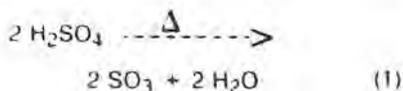
Conventional Incineration (Excess-Air Incineration)

Conventional incineration is the most common way of destroying hazardous substances. Numerous commercial hazardous waste incinerators are operating successfully throughout the United States and worldwide. Some of these operating systems are transportable, which makes them convenient for the destruction of hazardous wastes at specific sites.

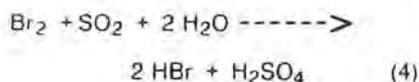
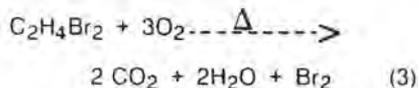
This process uses combustion to oxidize hazardous materials to harmless or less toxic materials. Products of incineration consist of combustion gases and, in some cases, solid residues. The combustion products usually require secondary treatment, such as wet scrubbing, particulate collection, or the use of afterburners. Unlike fluorine and chlorine, which generate primarily hydrogen halides upon combustion in excess air, brominated wastes generate bromine when incinerated, which is difficult to remove from the flue gases by currently operational gas-processing techniques. Caustic is typically used as the scrubbing medium in many hazardous waste incinerators; however, it is believed that a caustic solution may not remove bromine as readily as it does hydrogen bromide. Therefore, modification of the incinerator operating conditions (e.g., addition of sulfur) will be required to prevent significant amounts of bromine emission into the atmosphere.

Incineration in Presence of Sulfur Dioxide or Sulfur-Containing Waste

This option entails burning halogenated waste in a conventional incinerator in the presence of sulfur dioxide or sulfur-containing wastes. Under the incinerator operating conditions, sulfur dioxide reacts with the halogen produced during incineration to form hydrogen halide and sulfuric acid. During the Rollins test burn on EDB stock, 10 percent sulfuric acid (H₂SO₄) was used as the source of sulfur. Under the kiln conditions, the H₂SO₄ decomposes as follows (Equations 1 and 2):



At high temperatures, the equilibrium reaction is displaced to the right, which favors decomposition. The bromine resulting from oxidation of EDB reacts with SO_2 and water to form hydrogen bromide (HBr) and H_2SO_4 .



The resulting acids can be easily removed in the scrubbers, eliminating the problem of halogen emissions.

Starved-Air Incineration

This option uses the same equipment and entails the same process flow as the conventional incineration process. The only difference lies in the process conditions in the incinerator. Unlike conventional incineration, starved-air incineration uses less than stoichiometric quantities of air for combustion purposes.

The bromine/hydrogen bromide chemical equilibrium favors hydrogen bromide formation under reducing conditions (less oxygen) with high water vapor in the furnace. Because hydrogen bromide is more easily scrubbed than is bromine, the possibility of toxic emissions due to bromine is lessened. Thus, conceptually, starved-air incineration appears to have the potential to destroy brominated wastes.

Cement Kiln

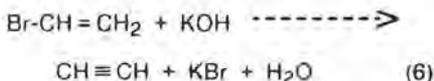
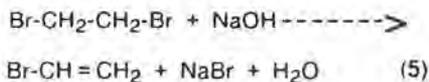
The primary cost factor in the production of cement is energy, which accounts for as much as 40 percent of the total cost. To offset escalating fuel costs, cement kilns use hazardous waste fuels; however, not all incinerable waste can be burned in a cement kiln. Cement kilns, which operate at 2000° to 2300°F, have a history of successful incineration

of chlorinated waste without any harmful emissions. The hydrogen chloride and chlorine generated in the furnace react with the raw materials (lime and some sodium and potassium in the ore) to form chloride salts. The alkaline conditions in the kiln cause the reactions to be rapid and complete. Thus, although many kilns are not equipped with wet scrubbing systems, the kiln acts as its own scrubber to minimize toxic emissions. Similar results are expected with brominated wastes.

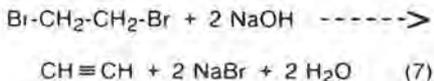
ATEG Process

The ATEG process, developed by the EPA involves a reaction between EDB and sodium hydroxide (NaOH) in the presence of a phase transfer catalyst, tetraethylene glycol (TEG) to yield acetylene, bromide salts, and water. Laboratory-scale studies on this reaction system were carried out by the EPA and the major findings were as follows:

- The reaction proceeds in two steps, with vinyl bromide as an intermediate product. A very small percentage of the vinyl bromide reacts further in the reactor to yield acetylene. The vinyl bromide had to be treated in a scrubber with the KTEG solution (KOH dissolved in TEG, diluted by water) to achieve complete conversion to acetylene. Thus, the reaction mechanism is as follows:



The overall reaction mechanism may be represented as follows:



- Laboratory tests seem to indicate relatively rapid reaction between the reactants
- Carbon disulfide (CS_2), a constituent of some of the pesticide formulations, was found to react quantitatively with the ATEG to form a viscous sludge

that inhibited the EDB destruction reaction

- Chloropicrin, a major constituent in some formulations, was found to react with the catalyst TEG, inhibiting the EDB destruction reaction

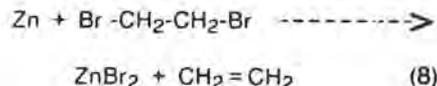
Therefore, the constituents that impede the reaction will have to be removed to successfully dispose of the pesticide formulations. It is believed that distillation of the CS_2 formulations should not be a problem, although distillation of chloropicrin formulations could be difficult. An advantage with distillation is that the products of distillation could be sold at market value and improve the overall process economics.

Based on the data available, a flow sheet was developed in consultation with the EPA. The process was proposed to be a batch operation consisting of a reactor, a packed bed scrubber (to treat reactor gases) system, and a reactor effluent dewatering (filters) and storage system. Preliminary process calculations and cost estimates were then developed to evaluate the process.

Two economic options have been considered for this process. The first involves building a completely new facility with all new equipment. The second involves using some process equipment available at the GARD facility (reactors, flare, and stack) to be used along with some new equipment.

Zinc Process

This process entails a classical organic reaction for the dehydrohalogenation of halogenated organics. Metallic zinc reacts with EDB at ambient temperatures to produce ethylene gas and zinc bromide. The reaction is represented as follows:



The reaction has been demonstrated only on a laboratory scale by the EPA. The Laboratory-scale studies resulted in 99+ percent EDB destruction. During these experiments, optimal results were obtained by using 100- to 200-mesh zinc powder slurried in distilled water and a little hydrochloric acid. The reaction temperature was not allowed to exceed 113°F.

The reaction is exothermic, with very high heat of reaction. It has been suggested that the reaction temperature

should be maintained below 113°F to avoid any possibility of runaway reactions.

Like the ATEG process, a conceptual flow sheet was developed for this process. It was proposed to operate the process as a batch operation. Preliminary process calculations and cost estimates were developed to evaluate the process.

Two capital investment alternatives are possible for this process. The first alternative entails the construction of a completely new facility with all new equipment. Under the second alternative, some equipment from the GARD facility would be used in conjunction with new equipment.

Results and Discussion

The results of the engineering evaluation are summarized in Table 1. From a technical standpoint, both starved-air incineration and destruction in an existing incineration facility without any modifications appear to be infeasible because of the bromine emissions that would exit through the stack.

Incineration in the presence of sulfur-containing waste holds an excellent promise for the elimination of bromine emissions. The test burn results show that this option meets the destruction standards for POHCs (DREs greater than 99.9999 percent) and emission standards (bromine below detection limits and bromide about 20 µg/dscf in the stack). Also, continuous monitoring data for CO₂, O₂, CO, NO_x, and SO₂ were reportedly well within the established standards. Bromine mass balance results seem to indicate that all the bromine exits the system in the scrubber water. Also, the fact that a currently operating incineration facility in Europe is successfully using this technology to destroy halogenated waste lends credibility to this option. Moreover, this option offers the advantage of speedy disposal of the entire EDB stock (probably less than a year) at a competitive cost. This is especially important in view of the urgency of the situation.

Cement kiln incineration appears to be a promising option; however, extensive testing would be required to establish the performance capabilities and optimal waste feed rates. The optimal waste feed rate would have to be determined so as to eliminate bromine emissions in the flue gases while not having an adverse effect on product quality. If the allowable feed rate was low, the overall time to complete the job would be higher. This,

in turn, could increase the overall cost of this option, however, no definitive estimates can be made until after test burns are performed.

The ATEG process has shown excellent capability to eliminate the EDB in bottoms obtained from the distillation of the CS₂ formulations. Previously the treatment of chloropicrin formulations with the ATEG process was regarded infeasible because of fear of forming unknown, and perhaps more hazardous compounds. However, preliminary tests seem to suggest that it may be possible to treat these formulations, without reacting the chloropicrin, by using a 30 percent caustic solution. This approach, however, needs further testing to prove its validity. The bench-scale tests seem to indicate that the presence of other constituents in the pesticide formulations interfere with the EDB destruction. Thus, extensive tests would also be required to study the feasibility of treating the miscellaneous formulations, without preprocessing them. Despite the promising results on the laboratory scale, the ATEG process could create operational problems because of its complexity. The process involves:

- A two step reaction.
- Number of reactants (NaOH, KOH, TEG).
- It is found to be sensitive to a number of operating parameters like the TEG concentration, caustic concentration, temperature, etc.
- Handling of potentially hazardous substances like vinyl bromide, etc.
- The process forms a wide range of byproducts, which could make disposal of the effluents difficult.

It is therefore evident that the process would need very extensive testing to eliminate uncertainties and operational difficulties and establish the optimal operating conditions, prior to design and scale-up. This could take considerable time, causing a delay in the overall disposal of the EDB pesticides.

Bench-scale tests with the zinc process show excellent promise with pure EDB. Disposal of the chloropicrin formulations seems to be a problem because of unacceptable levels of DREs, formation of unknown products, high zinc consumption, and high hydrochloric acid consumption. Reaction of zinc with the CS₂ formulations show that the carbon disulfide reacts rapidly with the zinc, resulting in very poor destruction of EDB. In all the tests with the zinc process, long reaction times were required to achieve

substantial EDB destruction. Even longer reaction times may be required to achieve 99.99 percent destructions. This could potentially make the process infeasible. Therefore, more tests would be required to determine

- Ways to achieve 99.99 percent destruction with all formulations, without any preprocessing. CS₂ may have to be removed prior to treatment.
- Ways to reduce the acid and zinc consumption, especially with the chloropicrin formulation.
- Feasibility of an azeotropic distillation of chloropicrin formulations using alcohol, as suggested by IT, if the 99.99 percent destruction of the formulation is not possible.
- The overall reaction time. This is an exothermic reaction. Thus, if the reaction rate is fast, then heat transfer will control the overall rate and vice versa. This will affect the process design and cost.

It is therefore evident that this process would need thorough pilot-plant testing to establish its feasibility and optimum operating conditions prior to design and scale-up. The process is more complex than previously envisaged.

Conclusion

At this point in time, incineration in the presence of sulfur dioxide seems to be the most viable and rapid way of disposing the pesticide formulations at a cost comparable to or lower than other methods. Successful trial burns for this method have been completed. As a result, the destruction process can be initiated immediately. The overall time for disposal should be less than six months. In view of the urgency for disposing of the pesticides, this process appears to be clearly the best choice.

The full report was submitted in partial fulfillment of Contract No. 68-03-3389 by PEI Associates, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

Table 1. Summary of Results of Engineering Evaluation

Criteria	Incineration in Presence of Sulfur Wastes	Starved-Air Incineration	Cement Kiln	ATEG	Zinc Process
Status	Commercial.	Not yet demonstrated.	Commercial.	Pilot plant. (Bench scale for EDB application).	Bench scale.
Accessibility	Accessible. Rollins has offered this technology.	Accessible. At least two facilities interested in pursuing this option.	Accessible. Two companies interested.	New plant to be built or existing plant to be modified	New plant to be built or existing plant to be modified.
Past experience	Trial burns at Rollins, Deerpark, TX, facility resulted in EDB destruction efficiencies greater than 99.999%. There was no visible bromine emissions at the stack. Preliminary results show that all bromine fed to the incinerator is captured in the scrubber system.	None for brominated waste.	One known test in Canada. Reports almost complete capture of bromine in the process residue.	Limited to bench-scale demonstration.	Limited to bench-scale demonstration.
Need for Development and Testing	In light of the successful trial burn, it is believed that no further development or testing is required.	The chemistry of bromine/HBr favors formation of bromine over HBr at ordinary operating conditions. Theoretically, this equilibrium can be shifted to yield HBr by reducing the oxygen and increasing the water vapor content. However, under partial pyrolysis, the extent of improvement in HBr formation is not known.	Minor modifications to kiln feed required. Process chemistry favors bromine capture in product without major changes in kiln design.	The development status of this technology will require more pilot-scale testing to establish feasibility, optimum operating procedures, and process parameters for design and scale-up.	The development status of this technology will require more pilot-scale testing to establish feasibility, optimum operating procedures, and process parameters for design and scale-up.
Pre-processing	Routine.	Routine.	Routine.	Carbon disulfide interferes with ATEG reaction. This will have to be removed by distillation. Chloropicrin may be difficult to treat with ATEG, and is not distilled easily. Thus, chloropicrin-containing formulations may have to be disposed of independently.	Carbon disulfide interferes with zinc reaction. It will have to be removed by distillation. Chloropicrin produces a coating on the zinc and may have to be removed by pre-processing.

Table 1. (Continued)

Criteria	Incineration in Presence of Sulfur Wastes	Starved-Air Incineration	Cement Kiln	ATEG	Zinc Process
Process Safety	Safe.	Safe.	Safe.	Acetylene is a major product of the process, which poses an explosion hazard. Also reaction is highly exothermic requiring careful control.	Ethylene and hydrogen are major reaction products, increasing explosion risks. Reactions are very exothermic requiring effective monitoring and control to avoid run away reactions.
Toxic Emissions	None, based on trial burn results.	Bromine emissions are possible.	Possibility of bromine emissions and partially oxidized organics.	Vinyl bromide and chloride emissions are possible.	Ethylene is reportedly herbicidal.
Residues	Brominated scrubber solution and sludges will require careful handling.	Brominated scrubber solution and sludges will require careful handling.	No problems envisioned.	Reactor effluents may be classified as a hazardous waste which will require appropriate handling and disposal. The residue contains byproducts of value which may be recovered prior to disposal.	Reactor effluents may be classified as a hazardous waste which will require appropriate handling and disposal. The residue contains byproducts of value which may be recovered prior to disposal.
Need for New/Additional Equipment	None.	New facility needs to be built or existing one modified.	None.	Build new facility or modify existing one.	Build new facility or modify existing one.
Extent of Corrosion	Corrosivity will be greater than that of chlorine, which is handled in existing facilities, and hence, may be a concern.	Corrosivity will be greater than that of chlorine, which is handled in existing facilities, and hence, may be a concern.	Due to the alkaline conditions in the kiln, corrosion is not expected to be a major problem.	Stainless steel material of construction is believed to be adequate. However, suitability of using SS needs to be established. FRP lined material could be a possibility.	Assuming that the problem of zinc coating (for chloropicrin formulation) can be solved without using excess HCl, there should be no problem of corrosion. However, if high acid consumption is required to cleanup the zinc surface, then corrosion could be a major concern.

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Table 1 (Continued)

Criteria	Incineration in Presence of Sulfur Wastes	Starved-Air Incineration	Cement Kiln	ATEG	Zinc Process
Process Compatibility with Pesticides	Compatible	Compatible	Compatible	Carbon disulfide in the formulations is incompatible with the TEG catalyst, which inhibits the main dehalogenation reaction.	Carbon disulfide reacts with zinc and will have to be removed to reduce high operating costs
Secondary Environmental Impact on Health Considerations	Bromine emissions of 0.1 ppm are known to be a health hazard. However, test burn results indicate no bromine emissions.	Bromine emissions of 0.1 ppm are known to be a health hazard.	Bromine emissions of 0.1 ppm are known to be a health hazard. In addition, secondary impact and health hazards can arise due to POHC's.	Possible due to vinyl bromide and chloride emissions. Both are known to be carcinogenic compounds.	Possible due to volatile organics from reaction mixture. Ethylene is known to affect plants and vegetation.
Mechanical Reliability	Reliable	Reliable	Reliable	Reliable.	Reliable.
Transportational Access to Facility	Available.	Railroad access available at some facilities. Mobile incinerators are available.	Railroad access available at least one willing facility.	To be determined.	To be determined.
Storage and Handling of Pesticide and Residue	No problems envisioned	No problems envisioned.	No problems envisioned.	No problems envisioned.	No problems envisioned.
Cost	Approximate range is 50 to 80 cents/lb	Unknown.	Approximately \$0.75-\$1.3/lb.	\$0.34 to \$0.78/lb ^a	\$0.3 to \$0.50/lb ^b
Permitting	Some facilities may require modification for EDB. Others may need to have new permits. Still others have the appropriate permits.	New permits would be required.	Permit modification required.	New permits or modifications required.	New permits or modifications required.
Probability of Success	Excellent. Incineration in presence of sulfur dioxide shows excellent promise. Results of recent test burn show no bromine emissions at the stack and DREs greater than 99.9999% for all POHCs	Fair. Test burns would be required to judge performance.	Good. Test burns would be required to judge performance.	Good. Pilot-scale testing required to establish feasibility and optimum operating conditions.	Good. Pilot-scale testing required to establish feasibility and optimum operating conditions.
Time Schedule for Completion	6 months or less	Approximately 1-1.2 to 2-1.2 years.	Depends on allowable feed. Approximately 1-1.2 years.	Approximately 2-1.2 years.	Approximately 2-1/2 years.

^a Cost excludes the cost for permitting, disposal of chloropicrin stock, and land lease. Also, since steam, water, and compressed air requirements are minimal, their contribution to operating cost was considered negligible. The amount of pesticide treated excludes the amount of chloropicrin formulation. Also, these cost figures are exclusive of development costs.

^b Cost has been calculated assuming that the problem of zinc coating with chloropicrin formulations can be solved without adding excess hydrochloric acid. Also, cost excludes the cost of permitting and land lease. Since steam, water, and compressed air requirements are minimal, their contribution to operating cost was considered negligible. The amount of pesticide treated includes the total amount of pesticide that needs to be destroyed. Also, these cost figures are exclusive of development costs.

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Edward R. Bates, is the EPA Project Officer (see below).

The complete report, entitled "Engineering Assessment of EDB Pesticide Destruction Technologies," (Order No. PB 89-110 118/AS; Cost: \$21.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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