

TEST BURNS FOR BANNED PESTICIDES*

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Summary

EPA's RREL-Cincinnati has been providing technical assistance to the EPA's Headquarters Office of Pesticide Programs (OPP) in recent years relative to the selection and implementation of proper, safe disposal of excess, cancelled and indemnified pesticides. Under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA, pre-1988 amendments), when EPA cancelled a pesticide due to findings of imminent health hazards associated with its intended use, EPA has been required to purchase all existing national stocks of the pesticide and become the responsible party or "waste generator" for the storage, treatment and disposal of the material. In all recent cases, the indemnified pesticide inventories became RCRA wastes and represented sizeable quantities. More importantly, for the recent pesticides; ethylene dibromide (EDB), dinoseb, and 2,4,5-T/Silvex, there appeared to be no safe, permitted, economical, and viable waste disposal method readily available. Thus, OPP elected to store the pesticides while assistance from ORD and outside contractors was solicited to identify workable options for disposal. Specifically, the problems concerned: coping with the bromine content in EDB, the significant nitrogen content representing a potential NO_x issue in the dinoseb, and the small but significant content of dioxin in the 2,4,5-T/Silvex. All of the foregoing concerns relate to the option of incineration of the pesticides. Though a host of other options were considered (recycling, chemical or biological treatment, deep well injection, etc.), incineration emerged as the most promising, near-term, and economically viable one, but one which required short-term research evaluations as described below before implementing.

Pesticides

EDB characteristics

Ethylene dibromide or EDB is a liquid halogenated hydrocarbon which was registered as a pesticide in 1948 and suspended in 1983. It was used largely in agriculture as a pre-plant soil fumigant and to fumigate stored grain. Human exposure to EDB resulted primarily from grain-based food products, and mounting evidence beginning as early as 1975 in terms of EDB's carcinogenic, mutagenic, and adverse reproductive effects ultimately led to suspension, can-

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cellation, and indemnification actions under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) by 1985. Indemnified stocks of various EDB formulations in the 1985–1988 time frame totalled approximately 329,000 gallons (3.7 million pounds) for which EPA was then responsible in terms of final disposal.

As with most pesticides, there existed a variety of individual EDB formulations with a range of concentrations of active ingredients and associated solvents for vehicles, etc. as well as a variety of sizes and types of containers, both pressurized and non-pressurized. Major constituents included ethylene dibromide (1.5 to 50 percent by weight or more), ethylene dichloride (up to 45 to 60%), carbon tetrachloride (16 to 80%), carbon disulfide (0 to 16%), sulfur dioxide (dissolved, 0 to 3%), chloropicrin (0 to 38%), and small amounts of diesel oil, naphtha, and pentane, etc., all expressed in terms of individual component weight percentages.

The most critical characteristic of EDB where incineration is concerned is its bromine content. The EDB molecule itself ($C_2H_4Br_2$) contains approximately 85% bromine by weight. Unlike chlorine, which readily combines with hydrogen to form scrubbable HCl, past experience with brominated compounds shows that thermal destruction will normally result in significant (and visible) bromine (gas Br_2) emissions from an incinerator stack.

Dinoseb characteristics

Dinoseb pesticides have been used for several decades primarily as contact herbicides to control broadleaf weeds, but also as a desiccant to dry vegetation on food crops in the fields to facilitate harvesting of vegetable and seed crops, etc. Dinoseb's active ingredient is an organo-nitrogen compound (2-sec-butyl-4,6-dinitrophenol) manufactured and formulated into over two dozen varieties of water and/or oil diluted forms, all liquid in nature, except for the "technical" or "parent acid" forms, which are dry solids. Some of dinoseb's challenging characteristics relative to disposal, beyond its high nitrogen content, are the explosive nature of the dry solids, the tendency for certain of the water-mixed formulations to precipitate solid salts of dinoseb upon exposure to sub-40°F (< 4°C) ambient temperatures, and the tendency for the organic solvent types of products to exhibit volatilization of their alcohol or other low boiling point vehicles if handled in open containers. However, water or oil dilution readily controls the explosion hazard issue for solids. In addition, many of the formulations contain significant amounts of sodium, calcium, and inert material, characterizing dinoseb as a "salt waste" and raising issues of refractory attack and attention to residue and particulates in terms of incineration. Neither heavy or toxic metals are involved, nor do dinoseb products (now wastes) contain chlorine, fortunately.

The human health risks associated with dinoseb are similar to the case with EDB. Dinoseb was suspended under an emergency order of October, 1986 and

then cancelled by EPA in June of 1988 because of evidence of causing possible birth defects, male sterility, and cancer. To date, EPA has received requests for disposal of some 2.7 million gallons (11×10^6 l) of liquid dinoseb and about 50,000 pounds (22,000 kg) of solid materials, and EPA anticipates ultimately receiving requests for disposal of a total of 4 million gallons of liquids.

Returning to the nitrogen issue, dinoseb's active ingredient molecule contains nearly 11% nitrogen by weight. Various diluted or formulated stocks contain from 1 to 6% nitrogen by weight, although the average nitrogen concentration of all stocks combined is closer to 1%. Most of the stocks are of the water-based types.

2,4,5-T/Silvex characteristics

With this liquid and solid pesticide, the primary concern is its low parts per billion dioxin content (a matter of incinerator permitting only), plus a secondary one of the unusually light-weight character of the material used as a carrier for the solid forms of the pesticide, vermiculite. Otherwise, existing incineration data for the POHCs involved gave EPA confidence that the waste is incinerable. There are 1 to 2 million pounds of solids and approximately 60,000 gallons of liquid inventories involved with 2,4,5-T/Silvex.

EPA's incineration programs

EDB

Initially, EPA considered incineration of EDB to be a low feasibility option due to the bromine gas release potential as noted above. The option of chemical treatment for the detoxification of EDB's major constituents and recovery of chemical feedstocks was initially selected and process development (including decanning of the majority of EDB stocks) was pursued under an EPA contract in the 1985-1987 time frame. Except for the decanning activity, this effort proceeded unsatisfactorily and the projected completion time and costs were soon deemed intolerable due to unforeseen process equipment scale-up problems.

In the fall of 1987, the incineration option was revisited as a direct result of an unsolicited proposal EPA received from a major commercial hazardous waste incineration firm. Proposed was the concept that the incineration of EDB along with adequate concentrations of sulfur (as S, SO₂, etc.) in the hot zone of the combustion chamber would encourage virtually complete chemical conversion of Br₂ to hydrogen bromide (HBr), which then should be scrubbed at high efficiency in the incinerator's emission control system. The effectiveness of the sulfur process, it was assured, had been functionally demonstrated on EDB materials in one of the proposer's incinerators in the past as verified by plume opacity observations, but no detailed stack gas verification analyses had been performed. On the issue of how sulfur enters the reactions to promote HBr,

EPA found that published literature existed on older laboratory studies which measured reaction rates etc. but these were conducted at temperatures much lower than in an incinerator's environment. The literature also offered no answer to what chemical reactions take place, and therefore offered no verification of the proposer's bromine control solution. EPA elected to evaluate the sulfur process at field-scale by investing in a detailed trial burn with test quantities of EDB, co-fired with a sulfur source in the form of 10 vol.% dilute sulfuric acid. This trial burn, conducted in December, 1987, was a complete success and the results are described below.

During the week of December 7, 1987, EPA conducted a detailed fieldscale trial burn of ethylene dibromide (EDB) at a permitted RCRA/TSCA commercial incineration facility owned by Rollins Environmental Services, Incorporated in Deer Park (Houston), Texas.

The three objectives for the test burn were:

1. To confirm the ability of the incinerator to achieve the levels of destruction and removal efficiency (DRE) for the principal hazardous components of the EDB materials.
2. To verify the effectiveness of sulfur addition to the combustion chamber to force the formation of hydrogen bromide (HBr).
3. To assess the compatibility of EDB co-firing with normal waste disposal operations at the facility.

The pesticide trial burn at the Rollins site consisted of 20,000 gallons of an EDB/ethylene dichloride (EDC)/ and carbon tetrachloride (CCl_4) mixture and 5,000 gallons of an EDB/chloropicrin formulation. Scoping tests, which were brief initial test firings of the EDB pesticides, were included as part of the trial burn program to immediately test the sulfur concept and to select pesticide flow rates to be used in the more detailed trial burn. Scoping tests showed good performance with various combinations of the two types of formulations, but the trial burn itself involved only non-chloropicrin material. The approximately 22,000 gallons of material remaining after completion of the scoping and trial burn program (including chloropicrin) was also incinerated at Rollins during the several days following the trial burn.

Table 1 is a summary of the test conditions used during the trial burn [1].

During the EDB trial burn, the incinerator achieved destruction and removal efficiencies and satisfied other regulatory standards as shown in Table 2 (as determined by VOST and M-5 methods).

During the scoping runs, the sulfur stream was intentionally stopped several times for brief periods (each stoppage lasted a few seconds only). A visible brownish plume resembling typical bromine fumes would issue forth from the stack whenever the sulfur stream was stopped. These momentary emissions, coupled with the reliable lack of visible or detectable bromine emissions with the sulfur present, demonstrated the effectiveness of the reaction in which Br_2 is converted to HBr by sulfur and then scrubbed in the air pollution control

TABLE 1

EDB waste stream composition (by weight)^a

| | |
|------------------|-------|
| EDB | 10.8% |
| EDC | 44.5% |
| CCl ₄ | 42.8% |

Pesticide flow rate into incinerator: 49.7–50.7 lb/min (fed to rotary kiln)

Net waste flow to incinerator: nominally 300 lb/min

| | |
|------------------------------|---------------------------------|
| kiln temperature | 1780–2000 °F (1100 °C) |
| afterburner temperature | 2230–2250 °F (1250 °C) |
| <i>Stack gas level</i> | |
| O ₂ | 10% |
| CO | 16–19 ppm |
| CO ₂ | 8–9% |
| NO _x ^b | 47–63 ppm (primarily NO) |
| SO ₂ | 42–46 ppm |
| flow rates | 39,800–43,000 dscf ^c |

^aIncluding a sulfur stream, PCB and RCRA solid and liquid waste streams.

^bDuring scoping tests, the chloropicrin material (38–40% EDB) was briefly fired at up to 40 lb/min and NO_x increased to 70–90 ppm in the stack.

^cdscf: dry standard cubic feet \cong 28.317 l

TABLE 2

Incinerator performance as determined by VOST and M-S methods

| | |
|------------------------|--|
| DRE: EDB | > 99.9999% |
| EDC | > 99.99999% |
| CCl ₄ | \cong 99.999–99.99999% |
| Particulate emissions | 0.0081–0.0123 grains per dscf ^a @ 7% CO ₂ |
| Bromine level in stack | non-detectable (detection limit 4–5 μ g per dscf) |
| Sulfur feed | 10–25 lb/min of a 10% dilute sulfuric acid solution (fired into the kiln next to the EDB gun) |

^adscf: dry standard cubic feet \cong 28.317 l.

device. Mass balance calculations to account for bromine at all entrance and exit and transient mass accumulation points associated with the incinerator showed that essentially all bromine was captured in the scrubber water streams.

Dinoseb

For Dinoseb, incineration immediately emerged as a priority disposal option for this RCRA P-020 type of waste, except that EPA felt it necessary to conduct pilot-scale tests to evaluate and quantify the DRE, NO_x and particulate gen-

eration and control issues. A secondary option, distillation for recovery of potentially salable chemicals was considered but not pursued due to the uncertain marketability of recovered materials plus the questionably long facility design, construction, and permitting time which would be required.

EPA conducted two pilot-scale, incineration test programs on dinoseb formulations during 1987, one at EPA's Research Triangle Park (RTP) facility in North Carolina and one at a contractor's facility in Tulsa, OK operated by the John Zink Company. Sampling and analyses and reporting for both studies were conducted by an EPA contractor, Acurex Incorporated. The results of these pilot-scale studies [2,3] are summarized in Tables 3 and 4.

The tests at RTP utilized a low-NO_x burner/package boiler simulator device with a nominal heat release capacity of 3 million Btu/h (30 GJ/h). Dynamyte 5 was fired as received at approximately 16.7 gallons per hour (60 l/h) in all tests. The firing techniques consisted of:

TABLE 3

Tests at RTP; the EPA facility in Research Triangle Park, NC

Objectives

- to determine DRE, NO_x and particulate emissions for the "Dynamyte 5" formulation of dinoseb, one of formulations with the highest concentration of dinoseb
- to obtain data with and without NO_x control via special burning techniques

Dynamyte 5 pesticide characteristics

| | |
|---------------------|--------------------------|
| dinoseb | 54.4% |
| diesel #2 oil | 4.04% |
| xylene | 32.5% |
| inerts | 9.6% |
| heating value (HHV) | 13,076 Btu/lb (60 MJ/kg) |
| nitrogen content | 6.63% by weight |

Results

| Test condition ^a | Temp. (°F) primary chamber | Temp. (°F) secondary chamber | NO _x ppm (corrected to 7% O ₂) |
|-----------------------------|-------------------------------|---------------------------------|---|
| conventional firing | 1306 | 1122 | 2998 |
| firing with air staging | 2450 | 1171 | 85 |
| air staging and reburning | 2104 | 1205 | 88 |

^aParticulate emissions 0.024-0.045 grains per or/dscf @ O₂ in all tests; DRE of dinoseb > 99.99% in all tests.

TABLE 4

Tests at the John Zink Company facility in Tulsa, OK

Objectives

- to incinerate a mixture of dinoseb blended from all inventories of different types of formulations proportioned approximately according to known volumes awaiting disposal
- to confirm DRE performance and quantify particulate emissions
- to quantify NO_x emissions under typical RCRA and TSCA operating temperatures
- to experience the handling, blending, and feeding characteristics of injecting a blend of dinoseb pesticides into a typical incinerator burner nozzle

The dinoseb mixture overall characteristics (wt.%)

| | |
|------------------------------------|-------------|
| Dyanap | 82 |
| Dynamyte 3 | 16 |
| Dynamyte 5 | 1.6 |
| net dinoseb and dinoseb salts | 21.2 |
| sodium ananap (Naptalam) | 19.0 |
| sodium hydroxide | 5.1 |
| water (primarily) and other inerts | 40.6 |
| xylene, alcohols, diesel oil, etc. | 13.5 |
| nitrogen content | ≈ 1 |
| overall heating value (HHV) | 4473 Btu/lb |

Results

| | |
|---|---|
| dinoseb mixture firing rates | 4-47 gal/h |
| DRE of dinoseb POHC | > 99.999% |
| NO _x emissions from natural gas alone | 92-150 ppm @ 7% O ₂ |
| NO _x emissions when firing dinoseb from low to high flow rates | 112-836 ppm @ 7% O ₂ at 1750° F |
| NO _x emissions when firing dinoseb with low flow rate | 274-307 ppm @ 7% O ₂ at 2200° F |
| NO _x emissions when firing dinoseb in a Noxidizer™ system | 40 ppm |
| particulate emissions before scrubber | 0.014-0.305 grains/dscf @ 7% O ₂ |
| particulate emissions after scrubber | 0.0025-0.0079 grains/dscf @ 7% O ₂ |

- Dynamyte 5 as the only fuel, with no special techniques to reduce NO_x;
- Dynamyte 5 as the only fuel, with air staging to reduce NO_x;
- Dynamyte 5 fired alone in the primary chamber, with both air staging and natural gas-fired reburning in secondary chamber to reduce NO_x.

2,4,5-T/Silvex

Thus far, ORD conducted the following brief tests relative to the solid forms of this pesticide:

- incinerating clean vermiculite of similar particle size in a pilot-scale electri-

cally heated infrared furnace, by using both dry vermiculite and vermiculite soaked with diesel oil;

- incinerating clean, dry vermiculite in EPA's mobile incinerator system (MIS).

The results of the above tests were intended to demonstrate in a preliminary way whether or not particle (vermiculite) carry-over from combustion chamber(s) into pollution control systems might be of concern.

RREL's testing to evaluate the issue of handling light vermiculite in two representative incinerator designs proved successful in that both types of units (infrared and the EPA mobile incinerator using rotary kiln, afterburner, and cyclone separator technology) were found to be effective in handling vermiculite.

Status of pesticide disposal

Based upon the field-scale EDB and the pilot-scale dinoseb incineration work described above, the Agency has been proceeding with incineration disposal of these pesticides. The current status as of early 1989 is that almost all of the EDB inventories have been incinerated and the entire task should be completed before spring. On dinoseb, incineration disposal contracts between EPA and two commercial incineration firms, Chemical Waste Management Inc. and Rollins Environmental Services Inc., were in place as of the end of 1988. Dinoseb incineration demonstration tests are anticipated shortly at up to five different sites. The demonstration tests which will involve firing representative quantities of waste coupled with observations of routine performance parameters plus NO_x measurements, if successful, are to be followed by routine incineration disposal. It is estimated that at least a 12 months time will be required to treat all of the dinoseb inventories.

Lastly, in the case of disposal of 2,4,5-T/Silvex, EPA currently feels confident that incineration in one or more existing commercial incinerators is feasible, except for the dioxin permitting issue. Whether an infrared unit such as the Shiro/Ecova types, or an ENSCO or EPA mobile type (which incorporate a post-incinerator chamber cyclone separator), or a large commercial unit (which has sufficient afterburner solids separation and containment space) is to be utilized is uncertain at this point. One of the most promising approaches at this juncture in the author's opinion appears to be to await the anticipated award of a dioxin permit to the Rollins Environmental Services incinerator at Deer Park, Texas.

References

- 1 RES(Tx) EDB Test Burn Program Emission Test Results, Final Reports, Vol. I and II. Alliance Technologies Corp., Bedford, MA, Alliance Project No. 5-879-999, June 1988.
- 2 EPA memorandum from William Linak, AEERL/CRB RTP to E.T. Oppelt, April 4, 1988. Results to Date of AEERL Dinoseb Tests, unpublished.
- 3 Test Report for the Trial Burn of Dinoseb in a Pilot-Scale Incinerator, September 20, 1989 (EPA and NTIS report numbers to be assigned).